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CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

PAGE

I.—*The Photochemical Decomposition of Nitrous Oxide and Nitric Oxide.* By JAMES YOUNGER MACDONALD . . . 1

II.—The Pressures produced on Inflammation of Mixtures of (*a*) Carbon Monoxide and Air, and (*b*) Hydrogen and Air in a Closed Spherical Vessel. By GEORGE BARTON MAXWELL and RICHARD VERNON WHEELER 15

III.—Glyoxaline-4(5)-formaldehyde. By WILFRED HUBBALL and FRANK LEE PYMAN 21

IV.—Syntheses in the Indole Series. Part II. 5 : 6-Benz-4-carboline and its Derivatives. By WILLIAM OGILVY KERMACK and ROBERT HENRY SLATER 32

V.—An Investigation of the Oxidation of Certain Aliphatic and Aromatic Carbon Compounds by Means of the Dichromate Reaction. By HARRY ARK 46

VI.—Studies in the Sterol Group. Part I. The Absorption Spectra of Some Cholesterol Derivatives. By ISIDOR MORRIS HEILBRON, RICHARD ALAN MORTON, and WILFRED ARCHIBALD SEXTON 47

VII.—Nor-*d*-ψ-ephedrine, an Alkaloid from *Ephedra* Species. By SYDNEY SMITH 51

VIII.—The Condensation of *cyclo*Hexanealdehyde and Malonic Acid. By SARBBANI SAHAY GUHA SIRCAR 54

IX.—A Cyclic Semipinacolin. By JAMES WILFRED COOK . 58

X.—Campnospermonol, a Ketonic Phenol from *Campnospermum brevipetiolatum.* By THOMAS GILBERT HENRY JONES and FRANK BERRY SMITH 65

XI.—Action of Beckmann's Chromic Acid Mixture on Some Monocyclic Terpenes. By THOMAS ANDERSON HENRY and HUMPHREY PAGET 70

XII.—The Cyanine Dyes. Part X. The Constitution of the *apo*Cyanines. By WILLIAM HOBSON MILLS and HENRY GEOFFREY ORDISH 81

XIII.—Stereoisomerism of Disulphoxides and Related Substances. Part II. Derivatives of 1 : 4-Dithian. By ERNEST VERE BELL and GEORGE MACDONALD BENNETT. 86

PAGE

XIV.—Some Analogous Organic Compounds of Phosphorus and Arsenic. By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON 92

XV.—The Resolution of Externally Compensated *p*-Nitrobenzoylalanine. By WILLIAM MORRIS COLLES and CHARLES STANLEY GIBSON 99

XVI.—The Stereochemistry of Reduced Quinoxalines. Part III. The Resolution of Externally Compensated α- and β-2 : 3 : 7-Trimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalines. By CHARLES STANLEY GIBSON, JOHN HENRY NUTLAND, and JOHN LIONEL SIMONSEN 108

XVII.—The Constitution of the Supposed *N*-Methylene-sulphurous Acid Derivative of Amines. Part I. Oxidation by an Alkaline Solution of Iodine. By GEORGE NEWBERY and MONTAGUE ALEXANDRA PHILLIPS . . 116

XVIII.—The Salting-out Effect. Influence of Electrolytes on the Solubility of *m*-Cresol in Water. By JOHN STANLEY CARTER and RICHARD KENNETH HARDY . . 127

XIX.—The Velocity Coefficient for Bimolecular Reactions in Solution. By RONALD G. W. NORRISH and FREDERICK F. P. SMITH 129

XX.—The Effect of the Constitution of a Chloroamine on its Hydrolysis Constant. By FREDERICK GEORGE SOPER and GILBERT FREEMAN SMITH 138

XXI.—Researches on Residual Affinity and Co-ordination. Part XXX. Complex *Ethylenethiocarbamido-salts* of Univalent and Bivalent Metals. By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL 143

XXII.—Observations on the Chlorination Products of ββ′-Dichlorodiethyl Sulphide. By STANLEY AUGUSTUS MUMFORD and JOHN WILLIAM COLE PHILLIPS 155

XXIII.—Studies in Colour and Constitution. Part II. Further Observations on the Effect of Substituents on the Colour of Azo-dyes. By HERBERT HENRY HODGSON and FREDERICK WILLIAM HANDLEY 162

XXIV.—The Reactivity of the Double Bond in Coumarins and Related αβ-Unsaturated Carbonyl Compounds. Part I. Addition of Cyanoacetamide to Coumarins. By TIRUVENKATA RAJENDRA SESHADRI 166

XXV.—The Formation of 2-Methylbenziminazoles. By MONTAGUE ALEXANDRA PHILLIPS 172

XXVI.—Optical Activity and the Polarity of Substituent Groups. Part VII. *sec.*-β-Octyl Esters of *o*-, *m*-, and *p*-Substituted Benzoic Acids. By H. GORDON RULE, WILLIAM HAY, ANNIE H. NUMBERS, and T. RAMSAY PATERSON 178

PAGE

XXVII.—*Applications of Thallium Compounds in Organic Chemistry. Part IV. Thallium Compounds of Polyhydroxy-compounds.* By ROBERT CHARLES MENZIES and MARGARET ELIZABETH KIESER 186

XXVIII.—Studies in Adjacent Substitution. Part I. Some Reactions of 3-Chloro-2-aminoanisole. By HERBERT HENRY HODGSON and ARNOLD KERSHAW 191

XXIX.—Triazole Compounds. Part II. Methylation of Some 1-Hydroxy-1 : 2 : 3-benztriazoles. By OSCAR L. BRADY and CEDRIC V. REYNOLDS 193

XXX.—The Structure of the Platinicyanides: The Potential of the Platino-Platinicyanide Electrode. By HENRY TERREY 202

XXXI.—The ψ-Cyanine Condensation. By FRANCIS MARY HAMER 206

XXXII.—The Reaction between Diaryloxy*iso*propyl Alcohols and Phosphorus Oxychloride in the Presence of Pyridine. By DAVID RUNCIMAN BOYD and DONALD ERNEST LADHAMS 215

XXXIII.—The Co-ordination Valency of Aluminium in its Salicylato-derivatives. By GEORGE JOSEPH BURROWS and IAN WILLIAM WARK 222

XXXIV.—The Migration of the Acyl Group in Partly Acylated Phenolic Compounds. Part I. By ARTHUR GEORGE PERKIN and RALPH CHARLES STOREY 229

XXXV.—Orientation Effects in the Diphenyl Series. Part V. The Independence of the Two Nuclei in Diphenyl Compounds. By RAYMOND JAMES WOOD LE FÈVRE and EUSTACE EBENEZER TURNER 245

XXXVI.—The Condensation of Certain β-Ketonic Esters with *o*-Hydroxymonostyryl Ketones. By ROWLAND HILL . 256

XXXVII.—The Hydrogen-ion Concentration of Aqueous Iodine Solutions. By HARRY MEDFORTH DAWSON . 259

XXXVIII.—The Parachor and Chemical Constitution. Part VII. Further Examples of Semipolar Double Bonds. By ADOLPH FREIMAN and SAMUEL SUGDEN 263

XXXIX.—The Solution Tension of Silver in Solvents other than Water. By FREDERICK KARL VICTOR KOCH . 269

XL.—The Effect of Catalysts on the Speed of Flame, Infra-red Emission, and Ionisation during the Combustion of Carbon Monoxide and Oxygen. By W. E. GARNER and C. H. JOHNSON 280

XLI.—A Chemical Method for preparing Carbon Hydrosol. By EUGEN CHIRNOAGA 298

PAGE

XLII.—The Electro-deposition of Indium with the Dropping-mercury Cathode. By SEISI TAKAGI 301

XLIII.—Studies of Valency. Part VIII. Extinction Coefficients and Molecular Conductivities of Vernon's Isomeric α- and β-Dimethyltelluronium Salts. The Molecular Structure of Quadrivalent Tellurium Compounds. By THOMAS MARTIN LOWRY, (Mrs.) ROSE R. GOLDSTEIN, and FRANK LATHE GILBERT 307

XLIV.—*cyclo*Telluropentane. By GILBERT T. MORGAN and HENRY BURGESS 321

XLV.—Nitrosation of Phenols. Part V. Preparation of an *o*-Nitrosophenol. By HERBERT HENRY HODGSON and JOHN SAMUEL WIGNALL 329

XLVI.—The Comparative Reactivities of Some Chloro-, Bromo-, and Iodo-nitrobenzenes. By ALBERT BREWIN and EUSTACE EBENEZER TURNER 332

XLVII.—The Mechanism of Activation of Halogen Atoms by a Nitro-group Present in the Same Aromatic Nucleus. By ALBERT BREWIN and EUSTACE EBENEZER TURNER . 334

XLVIII.—The Nitration of Benzaldoxime and Some of its Derivatives. By OSCAR L. BRADY and BRIAN E. M. MILLER 337

XLIX.—The Addition of Bromine to Ethylenic Compounds in Non-hydroxylic Solvents. By DAVID MATTHEW WILLIAMS and THOMAS CAMPBELL JAMES 343

L.—Studies in the Sterol Group. Part II. The Formation of ψ-Cholestene and Cholestenone by the Dry Distillation of Cholesterol. By ISIDOR MORRIS HEILBRON and WILFRED ARCHIBALD SEXTON 347

LI.—The Chlorination of Anilides. Part II. The Decomposition of *N*-Chloroacetanilide by Heat. By ALAN EDWIN BRADFIELD 351

LII.—Syntheses in the Phenazine Series. By HAMILTON McCOMBIE, HAROLD ARCHIBALD SCARBOROUGH, and WILLIAM ALEXANDER WATERS 353

LIII.—The Constituents of Indian Turpentine from *Pinus longifolia*, Roxb. Part IV. By P. PARAMESWARAN PILLAY and JOHN LIONEL SIMONSEN 359

LIV.—On the Possibility of Ring-chain Valency Tautomerism and of a Type of Mobile-hydrogen Tautomerism analogous to the Wagner–Meerwein Re-arrangement. Part I. Some Derivatives of Phorone. By CHRISTOPHER KELK INGOLD and CHARLES WILLIAM SHOPPEE . . . 365

PAGE

LV.—The Parachor and Chemical Constitution. Part VIII. Ring-chain Valency Tautomerism in Phorone Derivatives. By SAMUEL SUGDEN 410

LVI.—The Union of Benzoylacetonitrile with Organic Bases in the Presence of Salicylaldehyde. Part II. By PANCHAPAKESA KRISHNAMURTI 415

LVII.—The Nature of the Alternating Effect in Carbon Chains. Part XXIII. Anomalous Orientation by Halogens, and its Bearing on the Problem of the Ortho–Para Ratio, in Aromatic Substitution. By CHRISTOPHER KELK INGOLD and CHARLES CYRIL NORREY VASS . 417

LVIII.—The Nature of the Alternating Effect in Carbon Chains. Part XXIV. The Directive Action in Aromatic Substitution of Certain Groups containing Triple Linkings. By JOHN WILLIAM BAKER, KENNETH ERNEST COOPER, and CHRISTOPHER KELK INGOLD 426

LIX.—α-*iso*Propylglutaconic Acid. By KALVOI VENKATAKRISHNA HARIHARAN, KOTTIAZATH NARAYANA MENON, and JOHN LIONEL SIMONSEN 431

LX.—Hydrogenation of Cyclic Compounds under Pressure in Presence of Osmium and Other Catalysts. By V. S. SADIKOV and A. K. MIKHAILOV 438

LXI.—The Laws of Aromatic Substitution. Part VI. A Quantitative Method for the Rapid Determination of Isomeric Nitro-derivatives of Laterally Substituted Toluenes. By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES 448

LXII.—The Laws of Aromatic Substitution. Part VII. The Constitution and Substitution of Phenylnitromethane and Some of its Derivatives. By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES 453

LXIII.—The Alkylation of α-Cyano-β-alkylacrylic Esters and of α-Phenyl-β-alkylacrylonitriles. By JOHN ALEXANDER MCRAE and RICHARD HELMUTH FRED MANSKE . . 484

LXIV.—On Haber's Glass Cell. By WALTER SCOTT HUGHES 491

LXV.—Cyclic Organo-metallic Compounds. Part IV. Tellurylium Compounds (*continued*). By HARRY DUGALD KEITH DREW 506

LXVI.—Cyclic Organo-metallic Compounds. Part V. Phenoxselenine and Phenoxthionine from Phenoxtellurine. Selenylium and Thionylium Compounds. By HARRY DUGALD KEITH DREW 511

PAGE

LXVII.—Silver Nitrate Concentration Cells in Acetonitrile and Benzonitrile. By FREDERICK KARL VICTOR KOCH. 524

NOTES.—Allyl Hexoate and Octoate. By VENANCIO DEULOFEU 528

Composition of Bleaching Powder. By CHARLES T. KINGZETT 528

The Re-arrangement of Benzyl Phenyl Ether. By WALLACE FRANK SHORT 528

LXVIII.—The Isomerism of the Oximes. Part XXXIII. The Oximes of Opianic Acid and of Phthalic Anhydride. By OSCAR L. BRADY, LESLIE C. BAKER, RICHARD F. GOLDSTEIN, and SAMUEL HARRIS 529

LXIX.—Studies on Hydrogen Cyanide. Part I. Mercurio Methyl Cyanide and the Alleged Isomerides of Hydrogen Cyanide. By JOSEPH EDWARD COATES, LEONARD ERIC HINKEL, and THOMAS HUBER ANGEL 540

LXX.—Acid and Salt Effects in Catalysed Reactions. Part XII. The Water Catenary (H^+–H_2O–OH^-) in the Iodination of Acetone. By HARRY MEDFORTH DAWSON and ARTHUR KEY 543

LXXI.—Colloidal Platinum. Part III. Its Natural Acidity and its Coagulation by Acids. By STUART W. PENNYCUICK and R. J. BEST 551

LXXII.—The Budde Effect with a Mixture of Bromine Vapour and Air. By ERNEST BROWN and DAVID LEONARD CHAPMAN 560

LXXIII.—The Nitration of Benzylaniline. By JOSEPH REILLY, JOHN J. MOORE, and PETER J. DRUMM . . 563

LXXIV.—Trimethylplatinum Acetylacetone, a Volatile Platinum Compound. By ROBERT CHARLES MENZIES . 565

LXXV.—The Synthesis of *meso*-Alkyl and *meso*-Aryl Anthracene Derivatives. Part III. By EDWARD DE BARRY BARNETT and JAMES WILFRED COOK . . 566

LXXVI.—A Contribution to the Stereochemistry of Tervalent Nitrogen. By JOSEPH GILBERT JACKSON and JAMES KENNER 573

LXXVII.—Synthetical Experiments on the Aporphine Alkaloids. Part I. A Synthesis of 5 : 6-Dimethoxyaporphine. By JOHN MASSON GULLAND and ROBERT DOWNS HAWORTH 581

LXXVIII.—The Acetoacetic Ester Condensation. By MERVIN CLARENCE FRANKLIN and WALLACE FRANK SHORT . 591

PAGE

LXXIX.—Lead Subacetate Solution ("Goulard's Extract") and its Reaction with Phenols. By CHARLES STANLEY GIBSON and ERNEST MATTHEWS 596

LXXX.—The Bromination of *m*-Methoxycinnamic Acid. By HERBERT DAVIES and WILLIAM DAVIES . . . 602

LXXXI.—The Alkaline Hydrolysis of ω-Bromo- and ω-Chloronitrostyrenes. By ARTHUR THURLBY DANN, ALF HOWARD, and WILLIAM DAVIES 605

LXXXII.—Derivatives of γ-Xylose. A Study of Xylosemonoacetone and its Conversion into 2 : 3 : 5-Trimethyl γ-Xylonolactone. By WALTER NORMAN HAWORTH and CHARLES RAYMOND PORTER 611

LXXXIII.—Polysaccharides. Part I. The Structure of Inulin. By WALTER NORMAN HAWORTH and ABRAHAM LEARNER 619

LXXXIV.—Some Sulphur Derivatives of Aromatic Methyl Ethers. By HERBERT HENRY HODGSON and FREDERICK WILLIAM HANDLEY 625

LXXXV.—The Origin of the Spectrum of the Glow of Phosphorus. By HARRY JULIUS EMELÉUS and ROBERT HENRY PURCELL 628

LXXXVI.—The Introduction of the Triphenylmethyl Group into Phenols. By DAVID RUNCIMAN BOYD and DOUGLAS VERNON NELMAR HARDY 630

LXXXVII.—Stereoisomerism in Polycyclic Systems. Part IV. Two Stereoisomerides of 2 : 3 : 4 : 5 : 12 : 13-Hexahydroquinindene. By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT 639

LXXXVIII.—Optically Active Derivatives of Phenylaminoacetic Acid. By ALEX. MCKENZIE and NELLIE WALKER 646

LXXXIX.—Density and Electrostriction of Dilute Manganese Salt Solutions. By ALAN NEWTON CAMPBELL . 653

XC.—Equilibrium between Alcohols and Salts. Part II. By ELLIS LLOYD, CONRAD BEVAN BROWN, DAVID GLYNWYN ROBERT BONNELL, and WILLIAM JACOB JONES . . 658

XCI.—Studies of Dynamic Isomerism. Part XXVI. Consecutive Changes in the Mutarotation of Galactose. By GILBERT FREEMAN SMITH and THOMAS MARTIN LOWRY. 666

XCII.—The Competitive Interaction of Alkyl and Aryl Halides with Magnesium. By HERBERT WILLIAM RUDD and EUSTACE EBENEZER TURNER 686

XCIII.—The Nitration of Mixed *m*-Dihalogenobenzenes. By HORACE ALFRED MAYES and EUSTACE EBENEZER TURNER 691

PAGE

XCIV.—Derivatives of 1 : 3-Dithiolan and of 1 : 3-Dithian. By JOHN CHARLES ALEXANDER CHIVERS and SAMUEL SMILES 697

XCV.—The Condensation of Certain Aldehydes with Ketones of the Morphine Group. By JOHN MASSON GULLAND . 702

XCVI.—Cryoscopic Evidence of Compound Formation in Mixtures of Organic Liquids. By WALTER MATTHEW MADGIN, JOHN BUTTERY PEEL, and HENRY VINCENT AIRD BRISCOE 707

XCVII.—The Adsorption of Hydrogen Ions and its Effect on the Swelling and Electrical Charge of Gelatin. By BHUPENDRA NATH GHOSH 711

XCVIII.—Researches on Antimony. Part II. Derivatives of Tri-*p*-tolylstibine. By ARCHIBALD EDWIN GODDARD and VICTOR EMMANUEL YARSLEY 719

XCIX.—Some Properties and Reactions of β-Chloroethyl, β-Cyanoethyl, and β-Carbethoxyethyl Toluene-*p*-sulphonates, including an Extension of the Friedel–Crafts Reaction. By GEORGE ROGER CLEMO and ERIC WALTON 723

C.—Properties of Conjugated Compounds. Part IV. The Formation of Isomeric Additive Dibromides from Butadiene. By ERNEST HAROLD FARMER, CYRIL DUNN LAWRENCE, and JOCELYN FIELD THORPE 729

CI.—Selenium Oxyfluoride. By EDMUND BRYDGES RUDHALL PRIDEAUX and CHARLES BERESFORD COX 739

CII.—The Action of Bromine Water on Certain Olefinic Acids. By JOHN READ and WILLIAM GALLOWAY REID . . 745

NOTES.—A New Pipette. By H. NORMAN RIDYARD . . 749

A Reaction of Caryophyllene. By DAVID T. GIBSON . 750

CIII.—The Burning of Carbon Disulphide. Part II. The Velocity of the Uniform Movement of Flame in Carbon Disulphide–Second Combustible–Air Mixtures. By ALBERT GREVILLE WHITE 751

Spectra and Atoms. A Lecture delivered before the Chemical Society on February 23rd, 1928. By A. FOWLER, D.Sc., F.R.S. 764

CIV.—The Action of Cuprous Cyanide on Methyl Iodide. By ERNALD GEORGE JUSTINIAN HARTLEY . . . 780

CV.—Chloroamines as Halogenating Agents. Iodination by a Chloroamine and an Iodide. By ALAN EDWIN BRADFIELD, KENNEDY JOSEPH PREVITÉ ORTON, and IDRIS CHEER ROBERTS 782

CVI.—On the Chemical Individuality of Humulene. By A. CHASTON CHAPMAN 785

PAGE

VII.—Syntheses in the Indole Series. Part III. The Theory of Anhydronium Base Formation and the Constitution of Methosulphates, with some Observations on the Fluorescence of 5 : 6-Benz-4-carboline and its Derivatives. By WILLIAM OGILVY KERMACK and ROBERT HENRY SLATER 789

VIII.—Internal Equilibrium in Liquid Sulphur. Part I. By DALZIEL LLEWELLYN HAMMICK, WILFRID R. COUSINS, and EDWARD J. LANGFORD 797

X.—The Mechanism of the Degradation of Fatty Acids by Mould Fungi. Part I. By THOMAS KENNEDY WALKER and PHILIP DALTON COPPOCK 803

X.—A New Synthesis of 4-Amino-3-hydroxyphenylarsinic Acid. By ISIDORE ELKANAH BALABAN 809

XI.—An Examination of a Method of Estimating Iron and Sulphur in Sulphides of Iron. By PERCY LUCOCK ROBINSON, LEONARD ALFRED SAYCE, and JAMES STEVENSON 813

XII.—The Reaction between Monohydrated Ferric Oxide and Hydrogen Sulphide at 100°. By THOMAS GIBSON PEARSON and PERCY LUCOCK ROBINSON 814

XIII.—The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part II. The Hydrogenation of Conjugated Systems. By SERGUEY V. LEBEDEV and ANASTASIA O. YAKUBCHIK 823

XIV.—Equilibrium in the Binary Systems: Ethylenediamine–Phenols. By NIKOLAI ANTONOVICH PUSHIN and LJUDEVIT SLADOVIĆ 837

XV.—Differential Potentiometric Titration. Part I. Simple Method (Method I). By BERNARD CAVANAGH . . 843

XVI.—Differential Potentiometric Titration. Part II. Refined Methods (Methods II and III). By BERNARD CAVANAGH 855

XVII.—Autoxidation during Slow Combustion. By ERNEST WALTER JOHN MARDLES 872

XVIII.—The Absorption Spectra of Anthracene Derivatives. Part I. By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and THOMAS ERIC ELLISON . 885

IX.—The Complex Salts of Bivalent Platinum with $\alpha\beta\gamma$-Triaminopropane. By FREDERICK GEORGE MANN 890

X.—The Influence of Groups and Associated Rings on the Stability of Certain Heterocyclic Systems. Part IV. The Substituted Butyro- and Valero-lactones. By SARBBANI SAHAY GUHA SIRCAR 898

PAGE

CXXI.—Mobile-anion Tautomerism. Part I. A Preliminary Study of the Conditions of Activation of the Three-carbon System, and a Discussion of the Results in Relation to the Modes of Addition to Conjugated Systems. By HAROLD BURTON and CHRISTOPHER KELK INGOLD 904

CXXII.—The Constitution of Thebenine. By JOHN MASSON GULLAND and CYRIL JOSEPH VIRDEN 921

CXXIII.—The Intermolecular Condensation of Acetylmethylanthranilic Acid by Means of Phosphorus Pentachloride and the Formation of a Complex *iso*Cyanine Dye. By ISIDOR MORRIS HEILBRON, SYDNEY LOUIS HOLT, and FRANCIS NOEL KITCHEN 934

CXXIV.—The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part IV. The Establishment of the Structure of Selachyl and Batyl Alcohols as Monoglyceryl Ethers. By ISIDOR MORRIS HEILBRON and WILLIAM MORGAN OWENS 942

CXXV.—The System Sodium–Tin. By WILLIAM HUME-ROTHERY 947

CXXVI.—Orientation Effects in the Diphenyl Series. Part VI. The Supposed Isomerism of the Dinitrotolidines. By RAYMOND JAMES WOOD LE FÈVRE and EUSTACE EBENEZER TURNER 963

CXXVII.—Observations on the Passivity of Metals. By ERNEST SYDNEY HEDGES 969

CXXVIII.—Some Dinitroethylbenzenes. By OSCAR L. BRADY, JAMES N. E. DAY, and P. S. ALLAM . . 978

CXXIX.—Benzoic Esters and Electronic Affinities of Radicals. Part I. By AHMAD ZAKI 983

CXXX.—The Parachor and Chemical Constitution. Part IX. Boron Compounds. By JOSEPH JOHN ETRIDGE and SAMUEL SUGDEN 989

CXXXI.—A Further Case of the Spontaneous Resolution of Externally Compensated Mixtures. By LEONARD ANDERSON and DOUGLAS WILLIAM HILL 993

CXXXII.—The Chlorination of Anilides. Part III. *N*-Chlorination and *C*-Chlorination as Simultaneous Side Reactions. By KENNEDY JOSEPH PREVITÉ ORTON, FREDERICK GEORGE SOPER, and GWYN WILLIAMS . 998

CXXXIII.—The Chlorination of Anilides. Part IV. The Significance of Velocity Measurements in Relation to the Problem of Benzene Substitution. By ALAN EDWIN BRADFIELD and BRYNMOR JONES 1006

PAGE

CXXXIV.—Synthesis of Cyclic Compounds. Part II. Ethyl *r*- and *meso*-βγ-Diphenylbutane-ααδδ-tetracarboxylates. Synthesis of a Truxinic Acid. By ISRAEL VOGEL 1013

CXXXV.—The Constitution of Irigenin and Iridin. Part I. By WILSON BAKER 1022

ANNUAL GENERAL MEETING 1034

PRESIDENTIAL ADDRESS 1051

OBITUARY NOTICES 1056

CXXXVI.—The Oxidation of Nitrophenylcyanoacetates. Part II. By ARTHUR FAIRBOURNE and HAROLD RICHARD FAWSON 1077

CXXXVII.—The Mononitrobenzils and the Heteronuclear Dinitrobenzils. By FREDERICK DANIEL CHATTAWAY and EDWARD AUTY COULSON 1080

CXXXVIII.—The Condensation of Chloral with Substituted Phenols. By FREDERICK DANIEL CHATTAWAY and FERNANDO CALVET 1088

CXXXIX.—Imide Ring Closure in Derivatives of Diketosuccinic Acid Phenylosazone. By FREDERICK DANIEL CHATTAWAY and WILLIAM GERALD HUMPHREY . . 1094

CXL.—The Action of Nitrous Acid on Amino-compounds. Part I. Methylamine and Ammonia. By THOMAS WESTON JOHNS TAYLOR 1099

CXLI.—The Alkaloids of Some Indian Aconites (*A. Balfourii*, *A. deinorrhizum*, and "Chumbi Aconite"). By THOMAS ANDERSON HENRY and THOMAS MARVEL SHARP 1105

CXLII.—The Comparative Effects of the Nitro-, Carboxyl, and Sulphonic Acid Groups on the Hydrolysis of Aryl Halides. By WILLIAM DAVIES and EDNA SWALLOW WOOD 1122

CXLIII.—Synthetical Experiments on the Aporphine Group. Part II. A Synthesis of Bulbocapnine Methyl Ether. By JOHN MASSON GULLAND and ROBERT DOWNS HAWORTH 1132

CXLIV.—The Reaction of Bromine with Aliphatic Acids. Part II. The Relative Speeds of Bromination of Acetyl Bromide and Acetyl Chloride. By HERBERT BEN WATSON 1137

CXLV.—Cyclic Disulphides derived from Diphenyl. By HARRY JAMES BARBER and SAMUEL SMILES . . 1141

CXLVI.—The Photodecomposition of Triphenylmethyl. By SYDNEY THOMAS BOWDEN and WILLIAM JACOB JONES . 1149

PAGE

CXLVII.—*A Method for the Photographic Examination of Moving Flames.* By A. GREVILLE WHITE . . . 1159

CXLVIII.—On the Oxidation of *n*-Hexane. By MAX BRUNNER and ERIC KEIGHTLEY RIDEAL . . . 1162

CXLIX.—The Isomerism of the Styryl Alkyl Ketones. Part IV. 4-Hydroxy- and Some Derivatives of 2-Hydroxy-styryl Alkyl Ketones. By ALEXANDER MCGOOKIN and DONALD JAMES SINCLAIR 1170

CL.—Some Miscibility Relations of Acetic Anhydride. By DAVID CHARLES JONES and HAROLD FREDERICK BETTS 1177

CLI.—Some Physical Properties of Acetic Anhydride and Related Substances and their Constitutional Significance. By DAVID CHARLES JONES 1193

CLII.—Conversion of Hydroaromatic into Aromatic Compounds. Part II. Action of Bromine on 5-Chloro- and 5-Bromo-1-phenyl-Δ^4-*cyclo*hexen-3-one. By LEONARD ERIC HINKEL and DONALD HOLROYDE HEY 1200

CLIII.—The Inhibition of Esterification by Pyridine. By KENNETH CLAUDE BAILEY 1204

CLIV.—Some Experiments on Intensive Drying. By RONALD HERBERT PURCELL 1207

CLV.—The Determination of Volatile Matter in Coke. By FREDERICK JOHN EATON and STUART PEXTON . . 1215

CLVI.—The Nature of the Alternating Effect in Carbon Chains. Part XXV. The Mechanism of Aromatic Side-chain Substitution. By CHRISTOPHER KELK INGOLD and EUGENE ROTHSTEIN 1217

CLVII.—Ring Structure and Optical Relationships in the Mannose–Rhamnose–Lyxose Series of Sugars. Isolation of a New Form of Lyxose. By WALTER NORMAN HAWORTH and EDMUND LANGLEY HIRST 1221

CLVIII.—Equilibrium in Solutions. A Note on "The Activity Theory of Reaction Velocity." By W. F. KENRICK WYNNE-JONES 1230

CLIX.—Equilibrium in Electrolyte Solutions and the Reaction-velocity Equation. By FREDERICK GEORGE SOPER 1233

CLX.—The Conductivity of Copper Hydrosols. By HUMPHREY DESMOND MURRAY 1235

CLXI.—Acid and Salt Effects in Catalysed Reactions. Part XIII. Inert Salt Effects in the Catalytic Action of Acids. By HARRY MEDFORTH DAWSON and ARTHUR KEY 1239

PAGE

CLXII.—Acid and Salt Effects in Catalysed Reactions. Part XIV. The Influence of Inert Salts on the Catalytic Catenary for Acetic Acid–Acetate Mixtures. By HARRY MEDFORTH DAWSON and ARTHUR KEY . . 1248

CLXIII.—Reactions of Carbohydrazide. Part II. By ANDREW MILLER MUNRO and FORSYTH JAMES WILSON 1257

CLXIV.—The Complex Salts of β-Methyltrimethylenediamine with Bivalent Platinum. By FREDERICK GEORGE MANN 1261

CLXV.—*The Action of Aniline on d-Glutamic Acid.* By WILLIAM HERBERT GRAY. 1264

CLXVI.—The Tautomerism of *cyclo*Pentadienes. Part I. Some Derivatives of Methyl*cyclo*pentadiene. By FRANK ROBERT GOSS and CHRISTOPHER KELK INGOLD . 1268

CLXVII.—The Nature of the Alternating Effect in Carbon Chains. Part XXVI. The Nitration of ω-Chloro- and ω-Bromo-*p*-xylene. By CHRISTOPHER KELK INGOLD and EUGENE ROTHSTEIN 1278

CLXVIII.—The Nature of the Alternating Effect in Carbon Chains. Part XXVII. The Nitration of some Aromatic Phosphonium, Arsonium, and Stibonium Salts. By CHRISTOPHER KELK INGOLD, FLORENCE RUTH SHAW, and IAN STUART WILSON 1280

CLXIX.—Diphenylamine-*p*-arsinic Acid. By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON 1286

CLXX.—*Chelate Compounds of Thallium Dialkyl.* By ROBERT CHARLES MENZIES, NEVIL VINCENT SIDGWICK, ERIC F. CUTCLIFFE, and JOHN M. C. FOX 1288

CLXXI.—Molecular Dissymmetry Dependent on Restriction of Rotation about a Single Bond. Optically Active Benzenesulphonyl-8-nitro-1-naphthylglycine. By WILLIAM HOBSON MILLS and KENNETH ALLAN CALDWELL ELLIOTT 1291

CLXXII.—The Higher-boiling Constituents of the Essential Oil of Hops. By A. CHASTON CHAPMAN 1303

CLXXIII.—The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part IX. The Effect of the *spirocyclo*Pentane Grouping on the Five-carbon Intra-annular Tautomeric Nucleus. By FRANK ROBERT GOSS 1306

CLXXIV.—The Interaction of Benzoyl Chloride and Diazomethane together with a Discussion of the Reactions of the Diazenes. By WILLIAM BRADLEY and ROBERT ROBINSON 1310

PAGE

CLXXV.—The Hypothesis of Valency-deflexion. By CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE 1318

CLXXVI.—Experiments on Transmutation. By JOHN ALBERT NEWTON FRIEND 1321

CLXXVII.—Constituents of *Myoporum lætum*, Forst. (The "Ngaio".) Part III. The Oxide Rings of Ngaione. By FREDERICK HENRY McDOWALL 1324

CLXXVIII.—Action of Cuprous Hydride on Diazonium Salts. A Combined Sandmeyer–Gattermann Reaction. By PANCHANAN NEOGI and ANIL KRISHNA MITRA . . 1332

CLXXIX.—Studies of Dynamic Isomerism. Part XXVII. The Absorption Spectra of Prototropic Compounds. Physical Properties of the Stable and Labile Forms of Benzoylcamphor. By THOMAS MARTIN LOWRY, CHARLES ALEXANDER HAMILTON MACCONKEY, and HENRY BURGESS 1333

CLXXX.—Optical Activity and the Polarity of Substituent Groups. Part VIII. Growing-chain Effects and the *ortho*-Effect in Benzoic Esters. By H. GORDON RULE, WILLIAM HAY, and JACK PAUL 1347

CLXXXI.—The Preparation of 4 : 4′-Dinitrobenzil. By FREDERICK DANIEL CHATTAWAY and EDWARD AUTY COULSON 1361

CLXXXII.—The Nitration of Aromatic Thiocyanates and Selenocyanates. By FREDERICK CHALLENGER and ARNOLD THORNTON PETERS 1364

NOTES.—3 : 4 : 5 : 6-Tetrahydro-4-carboline. By JULIUS NICHOLSON ASHLEY and ROBERT ROBINSON . . 1376

The Occurrence of Titanium Tetrachloride in Commercial Disilicon Hexachloride. By FREDERIC STANLEY KIPPING and REGINALD AUBREY THOMPSON . . 1377

Fission of the Pyridine Nucleus by Oxidation with Alkaline Potassium Permanganate. By BRIAN DUNCAN SHAW and ARTHUR LESLIE WILKIE 1377

The Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. By ERWIN OTT . . 1378

Separation of Phthalic and Homophthalic Acids. By HARRY GORDON POOLE 1378

Arrhenius Memorial Lecture. Delivered on May 10th, 1928. By SIR JAMES WALKER, F.R.S. 1380

CLXXXIII.—The Dilution and Neutral-salt Errors of Buffer Mixtures. By CHARLES MORTON 1401

PAGE

CLXXXIV.—The Conductivities of Sodium and Potassium Derivatives of β-Ketonic Compounds in Alcoholic Solution. By EILEEN WHITE 1413

CLXXXV.—Some Thiazole Derivatives. Part II. By HERBERT WILLIAM STEPHEN and FORSYTH JAMES WILSON 1415

CLXXXVI.—The Mechanism of the Degradation of Fatty Acids by Mould Fungi. Part II. By PHILIP DALTON COPPOCK, VIRA SUBRAMANIAM, and THOMAS KENNEDY WALKER 1422

CLXXXVII.—Organic Derivatives of Silicon. Part XXXVI. Highly Complex Condensation Products of Diphenyl- and Di-*p*-tolyl-silicanediol. Fission of the Si–Ph Link. By FREDERIC STANLEY KIPPING and ARTHUR GEORGE MURRAY 1427

CLXXXVIII.—Organic Derivatives of Silicon. Part XXXVII. The Production of Tetrabenzylsilicane, Tribenzylsilicyl Oxide, and Other Products by the Action of Sodium on Dibenzylsilicon Dichloride. By ALFRED RAYMOND STEELE and FREDERIC STANLEY KIPPING . 1431

CLXXXIX.—The Catalytic Oxidation of Nitro- and Halogen Derivatives of Toluene by Means of Air. By EDWARD BRADFORD MAXTED and ARTHUR NORMAN DUNSBY. . 1439

CXC.—The Influence of Glass upon Vapour Pressure. By JACOBUS RINSE 1442

CXCI.—Reduction of Nitrites, Nitrates, and Nitric Acid with Magnesium Amalgam: A New Method of Preparing Hyponitrites. By PANCHANAN NEOGI and BIRENDRA LAL NANDI 1449

CXCII.—Experiments on the Synthesis of Anthocyanins. Part IV. The Constitution of *O*-Benzoylphloroglucinaldehyde. By ALEXANDER ROBERTSON, ROBERT ROBINSON, and ADA MARGARET STRUTHERS 1455

CXCIII.—Experiments on the Synthesis of Anthocyanins. Part V. A Synthesis of 3-β-Glucosidylpelargonidin Chloride, which is believed to be identical with Callistephin Chloride. By ALEXANDER ROBERTSON and ROBERT ROBINSON 1460

CXCIV.—Neocyanine. By FRANCES MARY HAMER . . 1472

CXCV.—The Isomeric 2-Amino-α-arylcinnamic Acids. By JOHN MASSON GULLAND and CYRIL JOSEPH VIRDEN . 1478

CXCVI.—The Action of Bromine Water on Certain Olefinic Hydrocarbons and Ethers. By JOHN READ and WILLIAM GALLOWAY REID 1487

PAGE

CXCVII.—*Optical Activity and the Polarity of Substituent* Groups. Part IX. Menthyl Esters of Methoxy-naphthoic and of Diphenyl-2-carboxylic Acids. By EGON BRETSCHER, H. GORDON RULE, and JOHN SPENCE 1493

CXCVIII.—Experiments on the Synthesis of Brazilin and Hæmatoxylin and their Derivatives. Part III. By WILLIAM HENRY PERKIN, jun., JNANENDRA NATH RÂY, and ROBERT ROBINSON 1504

CXCIX.—*The Action of Certain Dibromotetracarboxylic Esters on* the Sodium Derivatives of Ethyl Malonate, Ethyl Ethanetetracarboxylate, and Analogous Substances. By JOHN JOSEPH LENNON and WILLIAM HENRY PERKIN, jun. 1513

CC.—A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XV. The Synthesis of Cyanidin Chloride by Means of *O*-Benzoylphloroglucinaldehyde. By ALEXANDER ROBERTSON and ROBERT ROBINSON . . . 1526

CCI.—A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XVI. The Synthesis of Pelargonidin Chloride by Means of *O*-Benzoylphloroglucinaldehyde. By ALEXANDER ROBERTSON, ROBERT ROBINSON, and JIRO SUGIURA 1533

CCII.—A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XVII. The Synthesis of Peonidin Chloride by Means of *O*-Benzoylphloroglucinaldehyde. By SHINZO MURAKAMI and ROBERT ROBINSON . . . 1537

CCCIII.—A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XVIII. A Synthesis of Malvidin Chloride. By WILLIAM BRADLEY and ROBERT ROBINSON . . 1541

CCIV.—The Constitution of Phenolphthalein. Part I. Preparation of Some Compounds of the Phthalein Type. By HAKON LUND 1569

CCV.—A Quantitative Study of the Oxidation of Methyl Oleate and Elaidate by Hydrogen Peroxide in Presence of Acetic Acid. By THOMAS PERCY HILDITCH and COLIN HENRY LEA 1576

CCVI.—The Mechanism of Tautomeric Interchange and the Effect of Structure on Mobility and Equilibrium. Part II. Ring-Chain Tautomerism in its Relation to the Mutarotation of the Sugars. By JOHN WILLIAM BAKER 1583

CCVII.—Electrometric Titration Curves of Dibasic Acids. Part I. Normal Acids. By RICHARD GANE and CHRISTOPHER KELK INGOLD 1594

PAGE

CVIII.—The Influence of Arsenic on the Catalytic Activity of *Platinum for the Oxidation of Sulphur Dioxide.* By EDWARD BRADFORD MAXTED and ARTHUR NORMAN DUNSBY 1600

CIX.—On Selenium Tetrafluoride. By EDMUND BRYDGES RUDHALL PRIDEAUX and CHARLES BERESFORD COX . 1603

CX.—The Laws of Aromatic Substitution. Part VIII. By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES 1607

CXI.—The Action of Phosphorus Pentachloride on Homophthalic Acid. By WILLIAM DAVIES and HARRY GORDON POOLE 1616

CXII.—On Active Nitrogen. Part V. The Decay of the Nitrogen After-glow. By ERIC JOHN BAXTER WILLEY 1620

CXIII.—The Chemistry of the Three-carbon System. Part XVII. *cyclo*Hexylideneacetone and *cyclo*Hexylidenemethyl Ethyl Ketone. By ALFRED HENRY DICKINS, WILFRED EYNON HUGH, and GEORGE ARMAND ROBERT KON 1630

CXIV.—The *Condensation of Ketones with Ethyl* Acetoacetate. By LEONARD GEORGE JUPP, GEORGE ARMAND ROBERT KON, and EDWARD HUBERT LOCKTON . . 1638

CXV.—Properties of Conjugated Compounds. Part V. The Hydrogenation of Certain Extended Heterogeneous Systems. By JOHN TREVOR EVANS and ERNEST HAROLD FARMER 1644

CXVI.—Mobile Anion Tautomerism. Part II. A Complementary Study of the Mechanism of Anionotropic Change, with Special Reference to the Fate of the Mobile Anion. By HAROLD BURTON 1650

CXVII.—$\alpha\gamma$-Diamino-β-phenylpropane and Related Compounds of Pharmacological Interest. By JOSEPH GILBERT JACKSON and JAMES KENNER 1657

CXVIII.—Mobile Hydrogen Tautomerism analogous to the Wagner–Meerwein Re-arrangement. Part II. The Tautomerism of 1(or 5)-Hydroxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentan-5(or 1)-one and its Derivatives. By CHARLES WILLIAM SHOPPEE 1662

CXIX.—Anomalous Rotatory Dispersion from the Standpoint of the Drude Equation. By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS 1671

CXX.—Rotatory Dispersion: Intersections of Dispersion Curves and of Temperature–Rotation Curves. By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS 1696

PAGE

CCXXI.—A Study of the Anomalous Rotatory Dispersion of Configuratively Related Compounds. By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS . 1712

CCXXII.—The Rotatory Dispersion of Optically Active Co-ordination Compounds. By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS 1727

CCXXIII.—The Study of Moving Flames. By WILLIAM PAYMAN 1738

CCXXIV.—The Preparation and Properties of Selenophen and Certain Halogen Derivatives of Selenophen. By HENRY VINCENT AIRD BRISCOE and JOHN BUTTERY PEEL 1741

CCXXV.—Studies of Valency. Part IX. Molecular Structure of Thallium Salts. (*a*) Thallium Tri-iodide; (*b*) Alkyl Derivatives. By ARTHUR JOHN BERRY and THOMAS MARTIN LOWRY [with (Mrs.) R. R. GOLDSTEIN and F. L. GILBERT] 1748

CCXXVI.—The Influence of Constitution on the Stability of Racemates. By ALEXANDER FINDLAY and ALAN NEWTON CAMPBELL 1768

CCXXVII.—Cryoscopic Irregularities with Phenols. By GEORGE MAXWELL RICHARDSON and PHILIP WILFRED ROBERTSON 1775

CCXXVIII.—The Alkaline Hydrolysis of Esters in Aqueous Alcoholic Solution. Part II. The Interaction of Phenoxides and Aliphatic Esters. By ERIC STEPHEN GYNGELL 1784

CCXXIX.—Pseudo-ternary Systems containing Sulphur. Part III. The System Sulphur–Sulphur Monochloride. By DALZIEL LLEWELLYN HAMMICK and MICHAEL ZVEGINTZOV 1785

CCXXX.—Effects induced by the Phenyl Group. Part I. The Addition of Polar Reagents to Styrene and the Behaviour of the Halogenated Ethylbenzenes. By FRANK ASHWORTH and GEORGE NORMAN BURKHARDT. 1791

CCXXXI.—The Influence of the Intensity of Illumination on the Velocity of the Photochemical Union of Bromine and Hydrogen, and the Determination of the Mean Life of a Postulated Catalyst. By FRANK BRIERS and DAVID LEONARD CHAPMAN 1802

CCXXXII.—The Lupin Alkaloids. Part I. By GEORGE ROGER CLEMO and GRACE CUMMING LEITCH . . . 1811

CCXXXIII.—Neodymium Selenate. By JOHN ALBERT NEWTON FRIEND and ALBERT ARTHUR ROUND . . . 1820

PAGE

CCXXXIV.—The Synthesis of *meso*-Alkyl and *meso*-Aryl Anthracene Derivatives. Part IV. By EDWARD DE BARRY BARNETT and JOHN LAURENCE WILTSHIRE . 1822

CCXXXV.—The Rotatory Dispersion of Derivatives of Tartaric Acid. Part III. Diacetyltartaric Acid and its Esters. By PERCY CORLETT AUSTIN . . . 1825

CCXXXVI.—The Rotatory Dispersion of Derivatives of Tartaric Acid. Part IV. Propyl and Butyl Tartrates. By PERCY CORLETT AUSTIN 1831

CCXXXVII.—Synthetical Experiments on the Aporphine Alkaloids. Part III. A Synthesis of Corytuberine Dimethyl Ether. By JOHN MASSON GULLAND and ROBERT DOWNS HAWORTH 1834

CCXXXVIII.—Syntheses in the Diphenyl Series. By LEONARD ERIC HINKEL and DONALD HOLROYDE HEY. 1838

CCXXXIX.—Derivatives of 7 : 8 : 9 : 10-Tetrahydro-αβ-naphthacarbazole and of 8 : 9 : 10 . 11-Tetrahydro-α′β′-naphthacarbazole. By STEPHEN HELLICAR OAKESHOTT and SYDNEY GLENN PRESTON PLANT 1840

CCXL.—The Preparation and Properties of Pure Phosphorus Trioxide. By CHRISTINA CRUICKSHANK MILLER 1847

CCXLI.—The Action of Fluorine upon Aqueous Solntions of Chromium and Manganese Salts. By FRIEDRICH FICHTER and ERNST BRUNNER 1862

CCXLII.—On the Possibility of Ring-chain Valency Tautomerism, and of a Type of Mobile-hydrogen Tautomerism analogous to the Wagner-Meerwein Re-arrangement. Part III. Orientation of some Cyclic Derivatives of Phorone. By CHRISTOPHER KELK INGOLD and CHARLES WILLIAM SHOPPEE 1868

CCXLIII.—Dichloro-*o*-xylenes. By LEONARD ERIC HINKEL, ERNEST EDWARD AYLING, and LILIAN COLLIER BEVAN 1874

CCXLIV.—The Nitration of *m*-Fluorophenol. By HERBERT HENRY HODGSON and JOSEPH NIXON 1879

CCXLV.—Studies in Colour and Constitution. Part III. The Influence of the Methylthiol, Methoxy-, and Chlorine Groups on the Colours of the Nitrobenzaldehydephenylhydrazones. By HERBERT HENRY HODGSON and FREDERICK WILLIAM HANDLEY . . . 1882

CCXLVI.—The Influence of Intensive Drying on the System Nitrogen Peroxide–Nitric Oxide–Oxygen. By JOHN WILLIAM SMITH 1886

CCXLVII.—The Thermal Decomposition of Thiobenzanilide. By ARTHUR WILLIAM CHAPMAN 1894

PAGE

CCXLVIII.—The Action of Nitrous Acid on Amino-compounds. Part II. Aliphatic Amino-acids. By THOMAS WESTON JOHNS TAYLOR 1897

CCXLIX.—The Condensation of Hexahydrocarbazole and of Tetrahydropentindole with *cyclo*Pentanone Cyanohydrin. By SYDNEY GLENN PRESTON PLANT and DOROTHY MAY LYDDON RIPPON 1906

CCL.—The Molecular Configurations of Polynuclear Aromatic Compounds. Part VII. 5 : 5′-Dichlorodiphenyl-3 : 3′-dicarboxylic Acid. By FRED BRIDGES MCALISTER and JAMES KENNER 1913

CCLI.—The Apparent Hydration of Ions. Part I. The Densities and Viscosities of Saturated Solutions of Sodium and Potassium Chlorides in Hydrochloric Acid. By JOHN WILLIAM INGHAM 1917

CCLII.—The Influence of Structure on the Solubilities of Ethers. Part I. Aliphatic Ethers. By GEORGE MACDONALD BENNETT and WILLIAM GEORGE PHILIP . 1930

CCLIII.—The Influence of Structure on the Solubilities of Ethers. Part II. Some Cyclic Ethers. By GEORGE MACDONALD BENNETT and WILLIAM GEORGE PHILIP . 1937

CCLIV.—The Phosphorescent Combustion of Sulphur. By HARRY JULIUS EMELÉUS 1942

CCLV.—The Constitution of Magnesium Acetate Solutions. Part II. Evidence from Vapour Pressures. By E. A. GOODE, NOEL STANLEY BAYLISS, and ALBERT CHERBURY DAVID RIVETT 195

CCLVI.—The Addition of Halogens to Unsaturated Acids and Esters. Part I. The Addition of Equimolecular Mixtures of Bromine and Chlorine to Cinnamic Acid and its Derivatives in Non-hydroxylic Solvents. By NORMAN WILLIAM HANSON and THOMAS CAMPBELL JAMES 195

CCLVII.—Steric Hindrance in Reactions of Substituted Quinoxalines. By GEORGE MACDONALD BENNETT and GERVASE HEWITSON WILLIS 19

CCLVIII.—The Relative Reactivity of Methylene Groups in 1 : 3-Diketones. By ARTHUR BERTRAM EDMUND LOVETT and ELWYN ROBERTS 19

CCLIX.—The Mechanism of Tautomeric Interchange and the Effect of Structure on Mobility and Equilibrium. Part III. The Function of Alkaline and Acid Catalysts in the Mutarotation of some Derivatives of Tetramethyl Glucose. By JOHN WILLIAM BAKER . . . 19

PAGE

NOTES.—The Nature of the Deposit formed during the Electrolysis of Neutral and Alkaline Solutions with an Antimony Cathode. By JULIUS GRANT 1987

NN'-Diphenyl-*o*-phenylenediamine. By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON . 1988

The Action of Disilicon Hexachloride on Ether. By FREDERIC STANLEY KIPPING and REGINALD AUBREY THOMPSON 1989

2 : 4 : 7-Trinitrofluorenone. By FRANK BELL . . . 1990

Carbazole-1-carboxylic Acid. By EDWARD FULLER BRISCOE and SYDNEY GLENN PRESTON PLANT . . . 1990

CCLX.—The Electrokinetic Potential between the Solid and Liquid States of a Single Substance. By FRED FAIRBROTHER and FRANK WORMWELL 1991

CCLXI.—Studies of Valency. Part X. Electrometric Titration of Vernon's α- and β-Dimethyltelluronium Bases. By FRANK LATHE GILBERT and THOMAS MARTIN LOWRY 1997

CCLXII.—Syntheses of Cyclic Compounds. Part III. The Reduction of Some Unsaturated Cyano-esters by Moist Aluminium Amalgam. A New Synthesis of Mono-substituted Malonic Acids and of ββ'β'-Tetramethyladipic Acid. Further Evidence for the Multiplanar Configuration of the *cyclo*Heptane Ring. By ISRAEL VOGEL 2010

CCLXIII.—Syntheses of Cyclic Compounds. Part IV. The Catalytic Decomposition of Suberic Acid and the Preparation of Suberone directly from Mixtures of Suberic and Azelaic Acids. By ISRAEL VOGEL 2032

CCLXIV.—The Action of Diazo-salts on Aromatic Sulphonamides. Part II. The Mechanism of the Reaction and the Constitution of the Diazosulphonamides. By ARTHUR KEY and PAVITRA KUMAR DUTT . . . 2035

CCLXV.—The Decomposition of Acetyl Peroxide and the Mechanism of Kolbe's Electrosynthesis. By OSWALD JAMES WALKER 2040

CCLXVI.—The Adsorption of Vapours on an Amalgamated Platinum Surface. By JOHN WILLIAM SMITH . . 2045

CCLXVII.—Halogen Derivatives of *o*- and *p*-Azophenol. By LOUIS HUNTER and RONALD SIDNEY BARNES . 2051

CCLXVIII.—The Preparation of Some Halogenoaminophenols. Part I. Mixed Tetrahalogen Derivatives of *o*-Azophenol. Part II. Halogen Derivatives of *p*-Hydroxyazobenzene. By LOUIS HUNTER and RONALD SIDNEY BARNES 2058

PA[GE]

CCLXIX.—The Reaction between Acetylene and Sulphur at Temperatures up to 650°. By JOHN BUTTERY PEEL and PERCY LUCOCK ROBINSON . . . . . . 206[

CCLXX.—Derivatives of ψ-Indoxyl*spirocyclo*hexane. By RAYMOND LIVINGSTON BETTS and SYDNEY GLENN PRESTON PLANT 207

CCLXXI.—The Hydrolysis of Guanidine Carbonate. By JAMES BELL 207

CCLXXII.—Styrylpyrylium Salts. Part X. Anhydropyrylium Bases and *spiro*Pyrans derived from Dibenzyl Ketone. By ROBERT DICKINSON, ISIDOR MORRIS HEILBRON, and FLORENCE O'BRIEN 207

CCLXXIII.—Synthetical Experiments on the Aporphine Alkaloids. Part IV. A Synthesis of Morphothebaine Dimethyl Ether. By JOHN MASSON GULLAND and ROBERT DOWNS HAWORTH 208

CCLXXIV.—The Action of Magnesium Phenyl Bromide on Methyl *o*-Cyanobenzoate. 1 : 3-Diphenyldihydro*iso*indole. By DAVID RUNCIMAN BOYD and DONALD ERNEST LADHAMS 208

CCLXXV.—Striated Photographic Records of Explosion Waves. Part II. An Explanation of the Striæ. By COLIN CAMPBELL and ARTHUR CALVERT FINCH . 209

CCLXXVI.—Equilibrium Diagram of the System Antimony–Arsenic. By QASIM ALI MANSURI 210

CCLXXVII.—Colloidal Platinum. Part IV. The Existence of Hexahydroxyplatinic Acid in Colloidal Platinum Solutions. By STUART W. PENNYCUICK 210

CCLXXVIII.—The Pectin and Hemicelluloses of the Flax Plant. By STANLEY THOMAS HENDERSON. . . . 211

CCLXXIX.—Resolution of Racemic Chlorobromoacetic Acid. By HILMAR JOHANNES BACKER and HINDRIK WILLEM MOOK . . . . 212[

CCLXXX.—*N*-Methyl Derivatives of 2-Phenylnaphthylene-1 : 3-diamine. By CHARLES STANLEY GIBSON, WILLIAM SIMPSON KENTISH, and JOHN LIONEL SIMONSEN . . 213

CCLXXXI.—The Interaction of Cuprous Chloride and the Chromates of Potassium in a Solution of Sodium Chloride. By HUBERT JOHN PATRIDGE VENN and VERNON EDGE 214

CCLXXXII.—Acid and Salt Effects in Catalysed Reactions. Part XV. The Catalytic Activity of Hydrochloric Acid in the Hydrolysis of Ethyl Acetate. By HARRY MEDFORTH DAWSON and WILLIAM LOWSON . . 214

PAGE

CCLXXXIII.—Acid and Salt Effects in Catalysed Reactions. Part XVI. Catalytic Effects in the Iodination of Mesityl Oxide. By HARRY MEDFORTH DAWSON and ARTHUR KEY 2154

CCLXXXIV.—Hydrolysis in Solutions of Potassium Laurate as measured by Extraction with Benzene. By JAMES WILLIAM MCBAIN and MONROE EATON . . 2166

CCLXXXV.—The Rotatory Dispersion of Certain Isomeric Butyl Esters of *l*-Mandelic Acid. By CHARLES EDMUND WOOD, ALBERT EDWARD CHRISMAN, and SYDNEY DIGGARY NICHOLAS 2180

CCLXXXVI.—The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part III. The Hydrogenation of Conjugated Systems. By SERGUEY V. LEBEDEV and ANASTASIA O. YAKUBCHIK . . 2190

CCLXXXVII.—10-Chloro-5 : 10-dihydrophenarsazine and its Derivatives. Part VI. Compounds containing Two Nitrogen and Two Arsenic Atoms in Six- and Five-ringed Systems. By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON 2204

CCLXXXVIII.—By-products of the Gattermann Aldehyde Reaction. By FRANK BELL and THOMAS ANDERSON HENRY 2215

CCLXXXIX.—Polyiodide Equilibrium in Aqueous and Salt Solutions. By JOHN STANLEY CARTER 2227

CCXC.—The Laws of Aromatic Substitution. Part IX. By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES. 2230

CCXCI.—The Solubility of Potassium Ferricyanide in Water between 0° and 100°. By JOHN ALBERT NEWTON FRIEND and WILLIAM NELSON SMIRLES 2242

CCXCII.—Lithium Sulphite and some Derivatives. By JOHN ALBERT NEWTON FRIEND and DONALD WHITWORTH POUNDER 2245

CCXCIII.—The Nature of the Alternating Effect in Carbon Chains. Part XXVIII. The Preparation and some Properties of Benzyl Fluoride. By CHRISTOPHER KELK INGOLD and EDITH HILDA INGOLD 2249

CCXCIV.—The Nature of the Alternating Effect in Carbon Chains. Part XXIX. Further Experiments bearing on the Problem of the Ortho-Para Ratio in Aromatic Substitution. By CHRISTOPHER KELK INGOLD and CHARLES CYRIL NORREY VASS 2262

CCXCV.—Electrometric Titration Curves of Dibasic Acids. Part II. β-Substituted Glutaric Acids. By RICHARD GANE and CHRISTOPHER KELK INGOLD . . . 2267

PAGE

CCXCVI.—Nitration of 4-Halogeno-2-hydroxy- and 2-Halogeno-4-hydroxy-benzaldehydes. By HERBERT HENRY HODGSON and THOMAS ALFRED JENKINSON . . . 2272

CCXCVII.—The Quadrivalency of Selenium. Part I. 4-Carboxydiphenyl and *p*-Carboxyphenyl Methyl Selenoxides. By WILSON ROBINSON GAYTHWAITE, JOSEPH KENYON, and HENRY PHILLIPS 2280

CCXCVIII.—The Quadrivalency of Selenium. Part II. The Simple Halogen Derivatives and the Dihydroxide of 4-Acetamidodiphenyl Selenide. By WILSON ROBINSON GAYTHWAITE, JOSEPH KENYON, and HENRY PHILLIPS 2287

CCXCIX.—The Quadrivalency of Selenium. Part III. The Instability of the Compounds of Quadrivalent Selenium derived from Phenyl Methyl and Phenyl Ethyl Selenides and Phenyl- and *p*-Tolyl-selenoglycollic Acids. By OWEN KEMPSTER EDWARDS, WILSON ROBINSON GAYTHWAITE, JOSEPH KENYON, and HENRY PHILLIPS . 2293

CCC.—The Use of Toluenesulphonic Esters in Place of Halogen Esters in Malonic Ester Syntheses. By DAVID HENRY PEACOCK and PO THA 2303

CCCI.—Dibenzyl Ether as a Cryoscopic Solvent. By GEORGE MACDONALD BENNETT and GERVASE HEWITSON WILLIS 2305

CCCII.—Derivatives of 2-Phenyl-6-methyl-4-pyrone. The Non-resolution of 2-Phenyl-6-methyl-4-pyrone d-α-Bromocamphor-π-sulphonate. By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN 2307

CCCIII.—The Methylene Bases from 1-Methylbenzthiazole and 1-Methylbenzselenazole Methiodides; with a Note on the Preparation of 1-Substituted Benzthiazoles. By LESLIE MARSHALL CLARK 2313

CCCIV.—The Effects of the Spatial Position of Substituent Groups on Acidic Strength. By DONALD HOLROYDE HEY 2321

CCCV.—The Intermolecular Condensation of Styryl Ketones. Part II. Styryl Nonyl Ketone and the Formation of Dimerides. By ISIDOR MORRIS HEILBRON and FRANCIS IRVING 2323

CCCVI.—Ammonium Polysulphides, Hydrogen Pentasulphide, and the Thiocarbonic Acids. By HERBERT MILLS and PERCY LUCOCK ROBINSON 2326

CCCVII.—The Synthesis of 1-Phenanthrol. By JOHN BALDWIN SHOESMITH and ALEXANDER GUTHRIE . . 2332

PAGE

CVIII.—Alternating Reactive Positions in the Nucleus of *tert.*-Butylbenzene. By JOHN BALDWIN SHOESMITH and ALEXANDER MACKIE 2334

CIX.—The Molecular Configurations of Polynuclear Aromatic Compounds. Part VIII. 6 : 6′-Dimethoxydiphenic Acid. By JAMES KENNER and HAROLD AUGUSTUS TURNER 2340

CX.—The Chemistry of the Three-carbon System. Part XVIII. Quantitative Investigations on the Influence of Alkyl Substituents on the $\alpha\beta$–$\beta\gamma$ Change in Unsaturated Acids: Observations on the Reduction of Sorbic Acid, and a New Synthesis of Pyroterebic Acid. By ALAN AUGUST GOLDBERG and REGINALD PATRICK LINSTEAD . 2343

CXI.—On the Possibility of Ring-chain Valency Tautomerism and of a Type of Mobile-hydrogen Tautomerism analogous to the Wagner–Meerwein Rearrangement. Part IV. Substitution Reactions of some Cyclic Derivatives of Phorone. By CHARLES WILLIAM SHOPPEE. . 2360

CXII.—An Attempt to prepare Optically Active Derivatives of Quadrivalent Tin. By FREDERIC BARRY KIPPING 2365

CXIII.—Naphthylene 1 : 8-Disulphide. By WILLIAM BENNETT PRICE and SAMUEL SMILES 2372

CXIV.—Certain Aryl Arsenoxides and the Corresponding Dichloro- and Di-iodo-arsines. By GEORGE NEWBERY and MONTAGUE ALEXANDRA PHILLIPS 2375

CXV.—The Apparent Hydration of Ions. Part II. The Densities and Viscosities of some Mixed Aqueous Solutions of Lithium Chloride and Hydrochloric Acid. By JOHN WILLIAM INGHAM 2381

CXVI.—The Reduction of Selenious Acid. By LESLIE MARSHALL CLARK 2388

CXVII.—The Formation of 2-Substituted Benziminazoles. By MONTAGUE ALEXANDRA PHILLIPS 2393

CXVIII.—The Influence of Intensive Drying on Inner Equilibria. Part III. By ANDREAS SMITS 2399

CXIX.—The Densi-Tensimeter. By ANDREAS SMITS . 2409

CXX.—The Action of Substituted Aromatic Amines on Camphoric Anhydride. Bromo- and Iodo-camphoranilic Acids and Camphoro-bromo- and iodo-phenylimides. By MAHAN SINGH, RAM SINGH AHUJA, and KISHEN LAL . 2410

CXXI.—Studies in the Nitration of Substituted Tertiary Aromatic Amines. By GEORGE ROGER CLEMO and JAMES MUIR SMITH 2414

PAGE

CCCXXII.—The Reduction of *p*-Dimethylaminobenzaldehyde, and the Preparation of *p*-Dimethylaminobenzyl Alcohol. By GEORGE ROGER CLEMO and JAMES MUIR SMITH 2423

CCCXXIII.—Trypanocidal Action and Chemical Constitution. Part VIII. Derivatives of β-Aminoethyl- and γ-Aminopropyl-arsinic Acids. By GEORGE ALECK CROCKER GOUGH and HAROLD KING 2426

CCCXXIV.—The Walden Inversion. By HANS NICOLAI KELLERMAN RØRDAM 2447

CCCXXV.—Derivatives of Tetrahydrocarbazole. Part VII. Reactions of 3-Methyltetrahydrocarbazole, 6-Chlorotetrahydrocarbazole, and their Acyl Derivatives. By SYDNEY GLENN PRESTON PLANT and REGINALD JOHN ROSSER 2454

CCCXXVI.—The Decomposition of Bornyl Benzene- and Naphthalene-sulphonates by Heat. The Products of Hydrolysis of Bornyl and Menthyl Benzene- and Naphthalene-sulphonates. The Influence of Solvents on the Temperature of Decomposition of these Bornyl and Menthyl Sulphonates. By THOMAS STEWART PATTERSON and IRENE MARY MCALPINE 2464

CCCXXVII.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXV. Bornyl Benzene- and Naphthalene-sulphonates in Various Solvents. By THOMAS STEWART PATTERSON and IRENE MARY MCALPINE 2472

CCCXXVIII.—Equilibrium in the Binary Systems Cresols–Amines. By NIKOLAI ANTONOVITCH PUSHIN and LJUDEVIT SLADOVIĆ 2474

CCCXXIX.—A Resolution of Benzoin. By ISAAC VANCE HOPPER and FORSYTH JAMES WILSON 2483

CCCXXX.—The Nitration and Bromination of 4-Methylbenzophenone. By WILLIAM BLAKEY and HAROLD ARCHIBALD SCARBOROUGH 2489

CCCXXXI.—The Constituents of Some Indian Essential Oils. Part XXV. 1-α- and 1-β-Curcumenes. By B. SANJIVA RAO and JOHN LIONEL SIMONSEN 2496

CCCXXXII.—Equilibrium in the Systems $ZnSO_4$–Na_2SO_4–H_2O at 0° and 25°; $MnSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 35°; and $CoSO_4$–K_2SO_4–H_2O at 25°. By ROBERT MARTIN CAVEN and WILLIAM JOHNSTON 2506

PAGE

CCXXXIII.—The Chemistry of the Three-carbon System. Part XIX. The Homomesitones. By AILEEN EDITH ABBOTT, GEORGE ARMAND ROBERT KON, and RALPH DAVID SATCHELL 2514

CCXXXIV.—The Chemistry of Aromadendrene. Part I. By LINDSAY HEATHCOTE BRIGGS and WALLACE FRANK SHORT 2524

CCXXXV.—Chloro-*o*-xylenols. Part II. 3-Chloro-*o*-4-xylenol, the Dichloro-*o*-4-xylenols and 4 : 5-Dichloro-*o*-3-xylenol. By LEONARD ERIC HINKEL, ERNEST EDWARD AYLING, and LILIAN COLLIER BEVAN 2529

CCXXXVI.—The Conditions determining the Thermodynamic Stability of Cyanohydrins of Carbonyl Compounds. Part I. Some Effects of (*a*) Substitution in Aromatic Aldehydes and (*b*) Ring Formation. By ARTHUR LAPWORTH and RICHARD HELMUTH FRED MANSKE 2533

CCXXXVII.—A New Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part II. The Constitution of Nitro- and Amino-phenylphthalazones. By FREDERICK MAURICE ROWE and ESTHER LEVIN 2550

CCXXXVIII.—A New Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part III. Preparation of Phthalazine, Phthalazone, and Phthalimidine Derivatives from *m*-Nitroaniline. By FREDERICK MAURICE ROWE, MAHMED AHMED HIMMAT, and ESTHER LEVIN 2556

CCXXXIX.—Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXXII. The Resolution of Phenylbenzylcarbinol. By WILLIAM GERRARD and JOSEPH KENYON 2564

CCXL.—The Mobility of Symmetrical Triad (Prototropic) Systems. Part III. Three-carbon Prototropy in an αγ-Diphenylallyl Ether. By CHARLES WILLIAM SHOPPEE 2567

CCXLI.—Conditions of Formation of Rings attached to the *o*-, *m*-, and *p*-Positions of the Benzene Nucleus. Part III. By ALAN FRANCIS TITLEY 2571

CCXLII.—Stereoisomerism in Polycyclic Systems. Part V. By WILLIAM HENRY PERKIN, jun., and SYDNEY GLENN PRESTON PLANT 2583

CCXLIII.—Experiments on the Synthesis of Certain γ-Ketonic Acids Closely Allied to Balbiano's Acid. Part I. Synthesis of α-Methyl*cyclo*pentane-1 : 1-diacetic Acid, of the Lactone of α-Hydroxy-α-methyl*cyclo*pentane-1 : 1-diacetic Acid, and of 1-Acetyl*cyclo*pentane-1-acetic Acid. By JOGENDRA CHANDRA BARDHAN . 2591

PAGE

CCCXLIV.—Experiments on the Synthesis of Certain γ-Ketonic Acids Closely Allied to Balbiano's Acid. Part II. Syntheses of $\alpha\beta\beta$- and $\alpha\alpha\beta$-Trimethyl-lævulic Acids, of the Lactone of α'-Hydroxy-$\alpha\alpha\beta$-trimethylglutaric Acid, and of γ-Keto-$\alpha\beta\beta$-trimethylpropane-$\alpha\gamma$-dicarboxylic Acid (Balbiano's Acid). By JOGENDRA CHANDRA BARDHAN 2604

CCCXLV.—Attempts to Synthesise Norpinic Acid. By GEORGE ROGER CLEMO and KENNETH NORMAN WELCH . 2621

NOTES.—Note on an Improved Method of Preparing Selenophen. By HENRY VINCENT AIRD BRISCOE, JOHN BUTTERY PEEL, and PERCY LUCOCK ROBINSON . . 2628

The Preparation of Acetonecyanohydrin. By KENNETH NORMAN WELCH and GEORGE ROGER CLEMO . . . 2629

Apparatus for Chromic Anhydride Oxidations. By WALLACE FRANK SHORT 2630

CCCXLVI.—The Reaction between Nitrous Acid and Hydrogen Sulphide. By LANCELOT SALISBURY BAGSTER . 2631

CCCXLVII.—The Velocity of the Acid Hydrolysis of Cotton Cellulose by Hydrochloric Acid, Alone, and in Presence of Alkali Chloride. By EDWARD HUNTER 2643

CCCXLVIII.—Cobalt Allylamines: A Supposed Co-ordination Number of Eight for Cobalt. By WILLIAM RALPH BUCKNALL and WILLIAM WARDLAW 2648

CCCXLIX.—The Density of Boric Oxide Glass and the Atomic Weight of Boron. By ARNOLD COUSEN and WILLIAM ERNEST STEPHEN TURNER 2654

CCCL.—Studies in Valency. Part XI. Molecular Conductivities and Extinction Coefficients of Derivatives of *cyclo*Telluropentane. By FRANK LATHE GILBERT and THOMAS MARTIN LOWRY 2658

CCCLI.—An Investigation on the Ceria-Thoria Catalysts. By A. B. GOGGS 2667

CCCLII.—Studies in the Composition of Coal. Oil-yielding Constituents. By RONALD HOLROYD and RICHARD VERNON WHEELER 2669

CCCLIII.—A Synthesis of Behenolic Acid. By RAMAKANTA BHATTACHARYA, SHANKAR RAO SALETORE, and JOHN LIONEL SIMONSEN 2678

CCCLIV.—Polysaccharides. Part II. The Acetylation and Methylation of Starch. By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and JOHN IVOR WEBB . 2681

CCCLV.—Polysaccharides. Part III. The Molecular Complexity of Inulin. By HARRY DUGALD KEITH DREW and WALTER NORMAN HAWORTH 2690

PAGE

CCCLVI.—A Contribution to the Chemistry of Nitroso-compounds. By JOHN CAMPBELL EARL, FRANK CADWALLADER ELLSWORTH, EDWARD CHARLES SNELL JONES, and JAMES KENNER 2697

CCCLVII.—The 3-Halogeno-2-, -4-, and -6-aminophenols. By HERBERT HENRY HODGSON and ARNOLD KERSHAW. 2703

CCCLVIII.—Adsorption and Constitution: The Adsorption of Organic Acids on Animal Charcoal. By KENNETH MASSY GRIFFIN, HENRY LORIMER RICHARDSON, and PHILIP WILFRID ROBERTSON 2705

CCCLIX.—Polymerides of Aliphatic Chloroaldehydes. By FREDERICK DANIEL CHATTAWAY and EDWIN GEOFFREY KELLETT 2709

CCCLX.—The Formation of Liesegang Rings as a Periodic Coagulation Phenomenon. By ERNEST SYDNEY HEDGES and ROSALIND VENETIA HENLEY 2714

CCCLXI.—Co-ordination Compounds of Quinquevalent Molybdenum: Complex Thiocyanates. By ROBERT GILBERT JAMES and WILLIAM WARDLAW 2726

CCCLXII.—Attempted Resolution of Triethylenediamine-nickel Chloride. By WILLIAM RALPH BUCKNALL and WILLIAM WARDLAW 2739

CCCLXIII.—Complex Oxalates of Quinquevalent Molybdenum. By HENRY MILLS SPITTLE and WILLIAM WARDLAW 2742

CCCLXIV.—The Interaction of Chloral and 2:4:6-Tri-halogen-substituted Phenylhydrazines. By FREDERICK DANIEL CHATTAWAY and FRANCIS GEORGE DALDY . 2756

CCCLXV.—Metallic Derivatives of Hydroxy-esters. Part I. Copper and Nickel Derivatives of Methyl Salicylate. By BRIAN WILFRED DOAK and JOHN PACKER . . . 2763

CCCLXVI.—Investigations in the Diphenyl Series. Part VIII. Derivatives of 2-Amino- and 4-Amino-diphenyl. By FRANK BELL 2770

CCCLXVII.—The Interaction of Bromine with Acetic Anhydride. Part IV. Bromination and Chlorination compared. By HERBERT BEN WATSON and EMRYS HADDON ROBERTS 2779

CCCLXVIII.—Conversion of Hydroaromatic into Aromatic Compounds. Part III. 3:5-Dichloro-1-phenyl-$\Delta^{2:4}$-*cyclo*hexadiene and its Behaviour with Chlorine. By LEONARD ERIC HINKEL and DONALD HOLROYDE HEY . 2786

CCCLXIX.—A Study in the Formation of Gels. Vulcanised Oils. By B. C. J. G. KNIGHT and P. STAMBERGER . 2791

PAGE

CCCLXX.—Transannular Anionotropic Migrations. By James Wilfred Cook 2798

CCCLXXI.—The Catalytic Production of Polynuclear Compounds. Part I. By George Roger Clemo and Robert Spence 2811

CCCLXXII.—The Crystal Structure of Silver Subfluoride. By Henry Terrey and Hugh Diamond 2820

Notes.—The Oxidation of *n*-Hexane. By Max Brunner and Eric Keightley Rideal 2824

The Preparation of Cholestenone. By Wilfred Archibald Sexton 2825

The so-called Bisthiohydantoins of Frerichs, Förster, and Höller. By Herbert William Stephen and Forsyth James Wilson 2826

The Enolisation of Homophthalic Anhydrides. By Thomas Stevens Stevens and James Leggat Wilson 2827

Preparation of 4-Bromophthalic Acid. By Leslie Charles Baker 2829

CCCLXXIII.—The Photochemical Decomposition of Glyoxal. By Ronald G. W. Norrish and John G. A. Griffiths . 2829

CCCLXXIV.—On Active Nitrogen. Part VI. The Formation of Iron Nitride in the Iron–Nitrogen Arc. By Eric John Baxter Willey 2840

CCCLXXV.—Acid and Salt Effects in Catalysed Reactions. Part XVII. The Variation of the Catalytic Activity of an Acid with its Concentration, and the Determination of Ionisation Constants. By Harry Medforth Dawson, George Vincent Hall, and Arthur Key . 2844

CCCLXXVI.—The Reactions of Hydrogen Chloride with the Dioxides of Selenium and Tellurium between 0° and 170°. By Thomas Wallace Parker and Percy Lucock Robinson 2853

CCCLXXVII.—The Production of Thiophen by the Interaction of Acetylene and Carbon Disulphide. By Henry Vincent Aird Briscoe, John Buttery Peel, and Percy Lucock Robinson 2857

CCCLXXVIII.—*o*-Sulphinobenzoic Acid. By William Bennett Price and Samuel Smiles 2858

CCCLXXIX.—The Interaction of Ethyl Acetoacetate with Distyryl Ketones. Part IV. Selective Addition to Unsymmetrical Chlorodistyryl Ketones. By Isidor Morris Heilbron and Rowland Hill 2863

CCCLXXX.—The Heat of Adsorption of Oxygen on Charcoal. Part III. By Douglas McKie . . . 2870

PAGE

CCCLXXXI.—The Ionisation of Aromatic Nitro-compounds in Liquid Ammonia. Part II. By WILLIAM EDWARD GARNER and HENRY FRANK GILLBE 2889

CCCLXXXII.—The Acylation of Diazomethane. The Effects of Variations in the Conditions on the Extent of Formation of Chloroacetophenone from Benzoyl Chloride. By WILLIAM BRADLEY and GEROLD SCHWARZENBACH 2904

CCCLXXXIII.—The Condensation of Chloral with Anisic Acid, with *p*-Nitroanisole, and with 2 : 6-Dichloroquinol. By FREDERICK DANIEL CHATTAWAY and FERNANDO CALVET 2913

CCCLXXXIV.—The Constitution of Laurotetanine. By GEORGE BARGER and ROBERT SILBERSCHMIDT . . 2919

CCCLXXXV.—Some Substitution Products of Azobenzene. By JAMES BURNS, HAMILTON MCCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH 2928

CCCLXXXVI.—Determination of the Pressure and Density of Moist, Saturated Ammonium Bromide Vapour. By ANDREAS SMITS and RONALD PURCELL . . . 2936

CCCLXXXVII.—Determination of the Pressure and Density of Moist, Saturated Ammonium Chloride Vapour. By ANDREAS SMITS and WILHELMUS DE LANGE . . 2944

CCCLXXXVIII.—Adsorption of Vapour on a Quartz or a Glass Wall. By ANDREAS SMITS 2952

CCCLXXXIX.—A Phase Rule Investigation of Cupric Bromide in Aqueous and Hydrobromic Acid Solutions. By SYDNEY RAYMOND CARTER and NORMAN JOSEPH LANE MEGSON. 2954

CCCXC.—Studies in the Composition of Coal. The Rational Analysis of Coal. By WILFRED FRANCIS and RICHARD VERNON WHEELER 2967

CCCXCI.—The Addition of Halogens to Unsaturated Acids and Esters. Part II. The Addition of "Bromine Chloride" to Phenylpropiolic Acid. By NORMAN WILLIAM HANSON and THOMAS CAMPBELL JAMES 2979

CCCXCII.—Studies in Complex Salts. Part I. The Preparation and Properties of Some Selenitopentamminecobalt Salts. By HARRY LISTER RILEY. 2985

CCCXCIII.—Synthesis of Oxydehydrocorydaline. By JOSEPH BLAKE KOEPFLI and WILLIAM HENRY PERKIN, jun. 2989

PAGE

CCCXCIV.—The Dependence of Rotatory Power on Chemical Constitution. Part XXXIII. The Resolution of *dl-m*-Carboxyphenyl Ethyl Sulphoxide and of *dl-m*-Carboxyphenylethylsulphine-*p*-toluenesulphonylimine. By JOSEPH HOLLOWAY, JOSEPH KENYON, and HENRY PHILLIPS 3000

CCCXCV.—The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXVI. The Optical Activity of Malic Acid in the Presence of Sodium Molybdate. By THOMAS STEWART PATTERSON and CHARLES BUCHANAN 3006

CCCXCVI.—Aminobenzthiazoles. Part X. The Mobility of the 1-Amino-3-methylbenzthiazole System. By ROBERT FERGUS HUNTER and ERIC ROFE STYLES. . 3019

CCCXCVII.—The Interaction of Acids and Neutral Salts with Stannic Oxide and its Relation to Electrical Charge. By BHUPENDRA NATH GHOSH 3027

CCCXCVIII.—The Effect of the Spatial Position of Substituent Groups on Acidic Strength. By BERNHARD FLÜRSCHEIM 3039

CCCXCIX.—Pentanitroaniline. By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES 3041

CCCC.—The Synthesis of Four Amino-3-hydroxy-1 : 4-benz*iso*oxazines. By GEORGE NEWBERY and MONTAGUE ALEXANDRA PHILLIPS 3046

CCCCI.—Heterocyclic Compounds containing Arsenic. Part II. Derivatives of 1 : 4-Benz*iso*oxazine. By GEORGE NEWBERY, MONTAGUE ALEXANDRA PHILLIPS, and RALPH WILLIAM EWART STICKINGS 3051

CCCCII.—Heterocyclic Compounds containing Arsenic. Part III. Some Derivatives of 4-Amino-3-hydroxyphenylarsinic Acid. By ISIDORE ELKANAH BALABAN . 3066

CCCCIII.—The Chlorination of Anilides. Part V. The Significance of Velocity Measurements in Relation to the Problem of Benzene Substitution (*continued*). By ALAN EDWIN BRADFIELD and BRYNMOR JONES . . 3073

CCCCIV.—Strychnine and Brucine. Part VII. The Constitution of the Alkaloids discussed in Relation to the Hypothesis that Dinitrostrychol is an *iso*Quinoline Derivative. By REGINALD CLIFFORD FAWCETT, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON . 3082

NOTES.—The Acetylation of Diethylene Oxide. By MORNA MACLEOD 3092

The Nitration of o-Bromoacetanilide. By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON 3092

PAGE

CCCCV.—The Alkaloids of Some Indian Aconites. Part II. Pseudaconitine. By THOMAS MARVEL SHARP . . 3094

CCCCVI.—The Action of Bromine on Strontium Oxide and its Hydrates. By HORACE BARRATT DUNNICLIFF, HARNAM DAS SURI, and KISHEN LAL MALHOTRA . 3106

CCCCVII.—Selective Solvent Action. Part VII. Solubilities in Mixed Solvents. By NORA GREGG-WILSON and ROBERT WRIGHT 3111

CCCCVIII.—Synthetical Experiments in the *iso*Flavone Group. Part III. A Synthesis of Genistein. By WILSON BAKER and ROBERT ROBINSON . . . 3115

CCCCIX.—The Oxidation of Dipinene. By LINDSAY HEATHCOTE BRIGGS and WALLACE FRANK SHORT . . 3118

CCCCX.—The Reduction of Nitro-compounds by Aromatic Ketols. Part II. Some *o*-, *m*-, and *p*-Azoxy-compounds. By HUGH BRYAN NISBET 3121

CCCCXI.—Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part II. Mechanism of Exhaustive Methylation (*continued*). By CHRISTOPHER KELK INGOLD and CHARLES CYRIL NORREY VASS. 3125

CCCCXII.—Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part III. A Decomposition of Dialkylsulphones. By GEOFFREY WILLIAM FENTON and CHRISTOPHER KELK INGOLD . 3127

CCCCXIII.—Heterocyclic Compounds containing Arsenic. Part IV. Carbamido-derivatives of Arylarsinic Acids. By RALPH WILLIAM EWART STICKINGS . . . 3131

CCCCXIV.—Heterocyclic Compounds of Arsenic. Part V. Benziminazolearsinic Acids. By MONTAGUE ALEXANDRA PHILLIPS 3134

CCCCXV.—Glucosides. Part I. The Formation of Glucosides from 3 : 4 : 6-Triacetyl Glucose 1 : 2-Anhydride. By WILFRED JOHN HICKINBOTTOM 3140

CCCCXVI.—The Structure of the Normal Monosaccharides. Part V. Lyxose. By EDMUND LANGLEY HIRST and JAMES ANDREW BUCHAN SMITH 3147

CCCCXVII.—Hydroxy-derivatives of Thioxanthone Dioxide. By WILLIAM BENNETT PRICE and SAMUEL SMILES . 3154

CCCCXVIII.—Carbocyanine Dyes with Substituents attached to the Three-carbon Chain. By FRANCES MARY HAMER 3160

CCCCXIX.—Surface Oxidation of Aluminium, Tungsten, and Molybdenum. By LEONARD CHARLES BANNISTER 3163

PAGE

CCCCXX.—Studies of Dynamic Isomerism. Part XXVIII. Absorption Spectra of the Ketonic and Enolic Forms of an α-Diketone. By THOMAS MARTIN LOWRY, HENRI MOUREU, and CHARLES ALEXANDER HAMILTON MACCONKEY 3167

CCCCXXI.—Studies of Valency. Part XII. Isomeric Derivatives of Diethyl Telluride. By FRANK LATHE GILBERT and THOMAS MARTIN LOWRY 3179

CCCCXXII.—Stereoisomerism of Disulphoxides and Related Substances. Part III. Some Pairs of Aromatic Disulphoxides. By ERNEST VERE BELL and GEORGE MACDONALD BENNETT 3189

CCCCXXIII.—Degradation of Quaternary Ammonium Salts. Part I. By THOMAS STEVENS STEVENS, ELTON MARSHALL CREIGHTON, ALEXANDER BROWN GORDON, and MALCOLM MACNICOL 3193

CCCCXXIV.—Studies in the Composition of Coal. The Active-decomposition Point of Coal. By RONALD HOLROYD and RICHARD VERNON WHEELER . . . 3197

CCCCXXV.—Explosions in Closed Cylinders. Part I. Methane–Air Explosions in a Long Cylinder. Part II. The Effect of the Length of the Cylinder. By WILLIAM ANTHONY KIRKBY and RICHARD VERNON WHEELER . 3203

CCCCXXVI.—Explosions in Closed Cylinders. Part III. The Manner of Movement of Flame. By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and RICHARD VERNON WHEELER 3215

CCCCXXVII.—Acid and Salt Effects in Catalysed Reactions. Part XVIII. The Dynamics of Auto-catalysed Ester Hydrolysis. By HARRY MEDFORTH DAWSON and WILLIAM LOWSON 3218

CCCCXXVIII.—Stability of Ferrous Sulphate Solutions and their Use in Standardising Permanganate. By JOHN ALBERT NEWTON FRIEND and ERIC GEORGE KEMP PRITCHETT 3227

CCCCXXIX.—Note on the Rate of Photochemical Combination of Chlorine and Hydrogen in Glass Capillary Tubes. By DAVID LEONARD CHAPMAN and PHILIP POWELL GRIGG 3233

CCCCXXX.—Crystallography of the Aliphatic Dicarboxylic Acids. By WILLIAM AUGUSTUS CASPARI 3235

CCCCXXXI.—The Condensation of Dichloroacetaldehyde with Phenols. By FREDERICK DANIEL CHATTAWAY and ALEXANDER ALLAN MORRIS 3241

PAGE

CCCCXXXII.—Preparation of Diethylaminoethanol Esters of Diphenyl-2-carboxylic Acid and Derivatives. By FRANK BELL 3247

CCCCXXXIII.—The Interaction of Piperidine with Nitro- and Halogenonitro-derivatives of Xanthone and Diphenylene Oxide. By RAYMOND JAMES WOOD LE FÈVRE 3249

CCCCXXXIV.—Researches on Residual Affinity and Coordination. Part XXXI. Molybdyl Bis-β-diketones. By GILBERT T. MORGAN and REGINALD ARTHUR SALTER CASTELL 3252

CCCCXXXV.—The Inhibition of Chemical Reactions. Part II. The Mechanism of the Inhibition of Esterification by Alkaline Substances. By KENNETH CLAUDE BAILEY 3256

CCCCXXXVI.—The Rotation Dispersion and Circular Dichroïsm of Caryophyllene Nitrosite. By STOTHERD MITCHELL 3258

CCCCXXXVII.—Interactions of Seleninm Oxychloride and Phenols. By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL 3260

CCCXXXVIII.—The Electrical Conductivities of Some Uni-univalent Salts in Benzonitrile. Evidence for the Incomplete Dissociation of Strong Electrolytes and the Applicability of the Law of Mass Action to their Dissociation. By AUSTIN RAYMOND MARTIN 3270

NOTES.—A Gas Circulating Pump. By GUY BARR . . 3293

An Attempt to Prepare ψ-*iso*Indole. By GEOFFREY WILLIAM FENTON and CHRISTOPHER KELK INGOLD . 3295

Note on the Paper by Hartley and Barrett on "The Determination of the Density of Liquids." By JOHN GRINDLEY 3297

OBITUARY NOTICES. 3299

List of Physico-chemical Symbols adopted by the Chemical Society.
[See J.C.S., 1921, **119**, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms	e	
Diameter	d	
Radius	r	
Ratio of circumference to diameter	π	
Summation	Σ	
Variation	δ	
Total differential	d	
Partial differential	∂	

2. *Universal Constants.*

Acceleration due to gravity	g	
Mechanical equivalent of heat	J	
Avogadro's constant {number of molecules in 1 gram-molecule (mole)}	N	
Gas constant per mole	R	
Faraday's constant (number of coulombs per gram-equivalent of an ion)	F	
Charge on an electron	e	

3. *General Physics and Chemistry.*

Length	l	
Height	h	
Mass	m	
Time	t	
Volume	v, V	
Density (mass per unit volume)	d	D
Pressure	p, P	
Concentration	c, C	
Mole fraction	x	
Critical constants: pressure, volume, temperature (centigrade), temperature (absolute), density	p_c, v_c, t_c, T_c, d_c	
Reduced quantities: pressure, volume, temperature, density	p_r, v_r, t_r, T_r, d	
van der Waals's constants	a, b	
Fluidity	ϕ	
Viscosity	η	
Surface tension	γ	σ
Diffusion coefficient	Δ	
Atomic weight	A	
Molecular weight	M	
Velocity coefficient of reaction	k	
Equilibrium constant	$K, (K_c, K_p)$	
van't Hoff coefficient	i	
Degree of dissociation (electrolytic, thermal, etc.)	α	

4. *Heat and Thermodynamics.*

	Usual symbol.	Alternative symbol.
Temperature (centigrade)	t	θ
Temperature (absolute)	T	
Critical temperature	t_c, T_c	
Reduced temperature	t_r, T_r	
Critical solution temperature	t_{cs}, T_{cs}	
Quantity of heat	Q	
Entropy	S	
Specific heat	c	
Specific heat at constant pressure	c_p	
Specific heat at constant volume	c_v	
Ratio of specific heats, $c_p : c_v$	γ	
Molecular heat	C	
Molecular heat at constant pressure	C_p	
Molecular heat at constant volume	C_v	
Latent heat per gram	l	
Latent heat per mole	L	
Maximum work (diminution of free energy)	A	

5. *Optics.*

	Usual symbol.	Alternative symbol.
Wave-length of light	λ	
Refractive index	n	n_r
Specific refractive power (Gladstone and Dale)	r_G, $[r_G]_\lambda^{t^\circ}$	
Specific refractive power (Lorentz and Lorenz)	r_L, $[r_L]_\lambda^{t}$	
Molecular refractive power	R_G, R_L; $[R_G]_\lambda^{t^\circ}$, $[R_L]_\lambda^{t^\circ}$	
Angle of optical rotation	α	
Specific rotatory power	$[\alpha]$	
Molecular rotatory power	$M[\alpha]$	
Specific magnetic rotation	$[\omega]$	
Molecular magnetic rotation	$M[\omega]$	

6. *Electricity and Magnetism.*

	Usual symbol.	Alternative symbol.
Quantity of electricity	Q	
Current intensity	I	
Resistance	R	W
Electromotive force	E	
Electrode potential, or discharge potential of an ion	E	ϵ
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero	E_h, E_c	ϵ_h, ϵ_c
Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration	${}_0E_h$, ${}_0E_c$	${}_0\epsilon_h$, ${}_0\epsilon_c$
Dielectric constant	ϵ	
Conductivity (specific conductance)	κ	
Equivalent conductivity	Λ	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent	Λ_{10}, Λ_v, Λ_∞	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion	Λ_k, Λ_a	
Equivalent conductivity of specified ions...	Λ_K, Λ_{Cl}	
Molecular conductivity	μ	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.	U_k, U_a	
Transport number of kation and of anion ...	n_k, n_a	
Magnetic permeability	μ	
Magnetic susceptibility	κ	

List of Symbols, Arranged Alphabetically.

Symbol.	Name of quantity.
A	Atomic weight; maximum work.
a	Van der Waals's constant.
b	Van der Waals's constant.
C	Concentration; molecular heat.
c	Concentration; specific heat.
C_p, C_v	Molecular heat at constant pressure, and at constant volume.
c_p, c_v	Specific heat at constant pressure, and at constant volume.
D	Alternative symbol for density.
d	Diameter; total differential; density.
d_c	Critical density.
d	Reduced density.
E	Electromotive force; electrode potential.
e	Base of Napierian logarithms; charge on an electron.
E_h, E_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_0E_h, {}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
F	Faraday's constant (number of coulombs per gram-equivalent of an ion).
g	Acceleration due to gravity.
h	Height.
I	Current.
i	Van't Hoff's coefficient.
J	Mechanical equivalent of heat.
K	Equilibrium constant.
K_c, K_p	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
k	Velocity coefficient of reaction.
L	Latent heat per mole.
l	Length; latent heat per gram.
M	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
m	Mass.
N	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
n	Refractive index.

List of Symbols, Arranged Alphabetically—(continued).

Symbol.	Name of quantity.
n_k, n_a	Transport number of kation and of anion.
n_r	Refractive index (alternative symbol).
P	Pressure.
p	Pressure.
p_c, p_r	Critical pressure : reduced pressure.
Q	Quantity of heat; quantity of electricity.
R	*Gas constant per mole;* electrical resistance.
R_G, R_L	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
r	Radius.
r_G, r_L	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
S	Entropy.
T	Absolute temperature.
T_c	Critical temperature (on the absolute scale).
T_r	Reduced temperature (absolute).
$T_{c.s}$	Critical solution temperature (absolute).
t	Time; temperature (centigrade).
t_c	Critical temperature (centigrade).
$t_{c.s}$	Critical solution temperature (centigrade).
t_r	Reduced temperature (centigrade).
U_k, U_a	Velocity of kation and of anion in cm./sec. when the potential *gradient is* 1 volt *per* cm.
V	Volume.
v	Volume.
v_c, v_r	Critical volume : reduced volume.
W	Electrical resistance (alternative symbol).
x	Mole fraction.
α	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
γ	Surface tension; ratio of specific heats.
Δ	Diffusion coefficient.
δ	Variation.
∂	Partial differential.
ϵ	Electrode potential (alternative symbol); dielectric constant.
ϵ_h, ϵ	Electrode potential referred to the normal hydrogen or the *normal calomel electrode respectively*, the potential of which is taken as zero (alternative symbols).
${}_0\epsilon_h$, ${}_0\epsilon$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
η	Viscosity.
θ	Temperature (centigrade), (alternative symbol).
κ	Specific conductance (conductivity); magnetic susceptibility.
Λ	Equivalent conductivity.
Λ_{10}, Λ_v, Λ_∞	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
Λ_k, Λ_a	Equivalent conductivity of kation and of anion.
λ	Wave-length of light.
μ	Molecular conductivity; magnetic permeability.
π	Ratio of circumference to diameter.
Σ	Summation.
σ	Surface tension (alternative symbol).
ϕ	Fluidity.
$[\omega]$	Specific magnetic rotation.

JOURNAL

OF

THE CHEMICAL SOCIETY.

I.—*The Photochemical Decomposition of Nitrous Oxide and Nitric Oxide.*

By JAMES YOUNGER MACDONALD.

THE modes of decomposition of nitrous oxide by heat (Hinshelwood and Burk, *Proc. Roy. Soc.*, 1924, *A*, **106**, 284; Briner, Meiner, and Rothen, *Helv. Chim. Acta*, 1926, **9**, 409), by α-rays (Wourtzel, *Le Radium*, 1919, **11**, 332), and by the silent electric discharge (Joshi, *Trans. Faraday Soc.*, 1927, **23**, 227) have already been determined, and its photochemistry is of importance. Previous work on the subject has been done by Berthelot and Gaudechon (*Compt. rend.*, 1910, **150**, 1517) and by Regener and Warburg (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1904, 1228), who found that nitrogen peroxide was produced. It was considered advisable to extend their work, with a view to observe the quantum efficiency and to determine the mechanism of the decomposition.

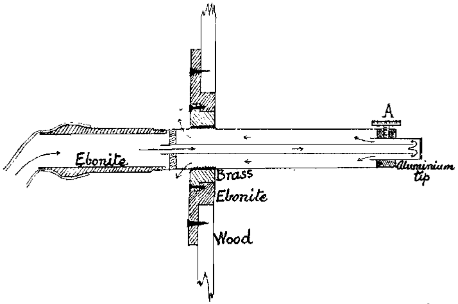
Nitric oxide also has been studied, although less exhaustively, by other workers. Briner and Boubnoff (*J. Chim. physique*, 1913, **11**, 597) investigated its decomposition under the combined influence of pressure and heat, and found that two actions took place, the major yielding nitrous oxide and oxygen, and the minor nitrogen and oxygen. Berthelot (*Compt. rend.*, 1876, **82**, 1360; 1910, **150**, 1517) ascertained that in the silent electric discharge nitrous oxide was produced, and on exposure to a mercury-vapour lamp, nitrogen and oxygen. A fuller study was undertaken in the hope that the results would be of use in the interpretation of the decomposition of nitrous oxide. These results, however, are not so complete as in the case of nitrous oxide, and their interpretation is more difficult.

EXPERIMENTAL.

The Activating Wave-length.—Preliminary experiments showed that nitrous oxide is decomposed by light of wave-length less than 2000 Å., which is strongly absorbed (compare Leifson, *Astrophys. J.*,

1926, **63**, 73). A new quartz mercury-vapour lamp produced considerable decomposition in 2 hours, nitrogen peroxide being formed. That this was due to the line 1849 Å. of the mercury arc and not to the Cario–Franck mechanism, involving the activation of mercury atoms which were accidentally present, was shown both by reducing the risk of contamination with mercury to a minimum, whereupon no corresponding decrease took place in the extent of decomposition, and by interposing in the path of the light a gelatin screen which absorbed all light below 2000 Å., and thereby stopped the decomposition. It was found, however, that after 20—30 hours' use the mercury-vapour lamp aged, and decomposition could no longer be produced by it. A condensed aluminium spark, whose

Fig. 1.



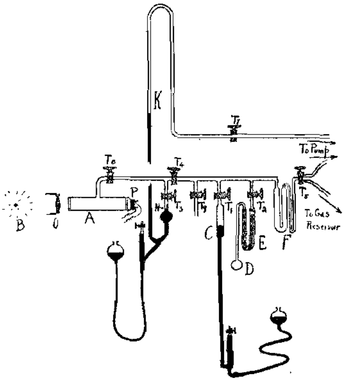
light is particularly rich in lines at 1860, 1930, and 1990 Å., was therefore substituted for it.

Apparatus.—The electrical circuit used was as follows. Alternating current at 100 volts, 15 amps., and 50 cycles was led from a rotary converter into a transformer and stepped up to 10,000 volts. It was then taken through high-frequency choke-coils (to protect the transformer from the high-frequency discharge) to the spark-gap, in parallel with which was a battery of condensers of total capacity 0·05 microfarad. The spark-gap was 1 cm. wide. Considerable difficulty was found in constructing efficiently cooled electrodes. These were finally made of 1-inch brass tube, being tipped with an aluminium cap turned out of ½-inch rod, each being cooled by a blast of air blown through an inner brass tube and returning through the annular space between this and the outer tube. A section of one of these electrodes is shown in Fig. 1, the

arrows indicating the current of air. All connexions in the condenser–spark-gap circuit were made of heavy copper strip, to minimise the energy loss due to heating, which would otherwise have been considerable. The circuit was regulated both by means of a low-frequency choke-coil, with a variable magnetic gap, in the primary alternating circuit, and by rheostats on the direct-current circuit which fed the rotary converter.

Two reaction vessels of different types were used. Vessel A was of quartz, test-tube shaped and ground into a glass socket, and was about 3 cm. in diameter and 17 cm. in length. It was laid hori-

FIG. 2.



zontally above the spark, 7·3 cm. from the electrodes, and was cooled by a draught of air. In spite of this, the temperature rose to about 40°, and all experiments with this vessel were carried out at that temperature. Such a vessel, having a comparatively large area exposed to the light, was suitable for experiments in which a considerable rate of decomposition was desired. Its shape, however, rendered it impossible to make any measurements of the light absorbed when using it, or to regulate the temperature accurately. Reaction vessel B consisted of a glass tube, 3 cm. in diameter and 15 cm. in length, with fluorite windows cemented to each end, and was cooled in a trough of water (see A, Fig. 2). The light was concentrated by a fluorite lens, O, and sent through the vessel in a

beam which was as nearly as possible parallel. A large-surface thermopile, P, was placed close to the second window.

As the analyses were based largely on pressure changes, it was necessary to use a pressure gauge in which nitrogen peroxide (formed in the reaction) did not come into contact with mercury. An all-glass gauge of the type described by Jackson (J., 1911, **99**, 1066) was at first employed, but as its accuracy was limited to about 1 mm. pressure, it was discarded in favour of the mercury manometer K (Fig. 2), in which the taps T_8 and T_3 maintained between the mercury surface and the reaction vessel an effective buffer of the gas being studied. By using a small microscope to set the mercury surface to the inserted glass pointer, N, and reading the height of the other column by a cathetometer, an accuracy of 0·1 mm. could be attained.

Analysis of the Products.—The method of procedure may be followed by reference to Fig. 2. It differed only in detail for the two gases studied. In both cases the purified gas was introdnced through T_5 into the apparatus, until approximately the required pressure was present, the bulb D being kept evacuated. Fine adjustments of pressure could be made by altering the level of the mercury in C. All taps were closed, and the reaction vessel was exposed to the light for the required period. T_8 and T_3 were then opened, and the change of pressure resultant upon the exposure was measured, a correction being applied for the dead space between T_8 and the mercury surface. Next, liquid air was placed round the double U-tube F, and the permanent gases were pumped off through T_5 by means of a Langmuir mercury diffusion pump backed by a Töpler pump. The gases so removed were collected. When nitrous oxide was being studied, these consisted of nitrogen and oxygen. They were measured together, and subsequently measured again after treatment with pyrogallol. In the case of nitric oxide, nitrogen and a small proportion of the undecomposed nitric oxide were removed in the first few minutes' pumping, and, after treatment with ferrous sulphate to remove the nitric oxide, the nitrogen was measured. The remainder of the nitric oxide was then pumped off, the rate of evaporation being 20—30 c.c. per hour. The gases retained by the liquid air consisted of nitrous oxide (in large excess, when this was the substance studied), nitrogen peroxide, and nitrogen trioxide. When the all-glass gauge was used, the pressure of the residual gases was measured, but this could not be done when the mercury manometer was employed. Nitrogen peroxide was next removed by distilling the mixture through tubes of solid caustic soda E, D being immersed in liquid air. In a number of the experiments, any nitrogen trioxide present was first

converted into peroxide by the addition of air, and the nitrous oxide which remained was then estimated from its pressure. When the amount of nitrous oxide was small, however, no air was admitted, and after passage through the caustic soda tubes the residual gas was pumped off and measured, nitric oxide produced from the decomposition of the trioxide being removed by ferrous sulphate.

It is sometimes stated (*e.g.*, Partington, "Text-book of Inorganic Chemistry," 1921, p. 588) that, although nitrogen trioxide is dissociated at room temperature into nitric oxide and nitrogen peroxide almost completely, the mixed gases are entirely absorbed by solid caustic soda, forming nitrite only, and thus acting as the trioxide. Nitric oxide was always found in the gas finally pumped off, however, indicating either that it is not completely absorbed in the presence of an equivalent of nitrogen peroxide, or that the mixture condensed in the liquid-air trap contains more than an equivalent of nitric oxide.

The nitrous oxide used in these experiments was obtained from cylinders, and was purified by passage over solid caustic soda and phosphorus pentoxide, and by fractionation from a liquid-air trap. The nitric oxide was prepared by the Lunge "nitrometer" reaction, and was pumped off from liquid air into the vessel in which it was stored.

Results with Nitrous Oxide.

The results of many analyses show that, under the conditions employed (*i.e.*, at 21·7—607 mm. pressure, at temperatures of 0—40°, and with times of exposure of 2—66·5 mins.), the final products consist almost entirely of nitrogen, nitrogen peroxide, and unchanged nitrous oxide. There is always, however, a little oxygen in the gas pumped off. Table I gives the results of two typical experiments at 15°, and serves to show the order of accuracy attained.

TABLE I.

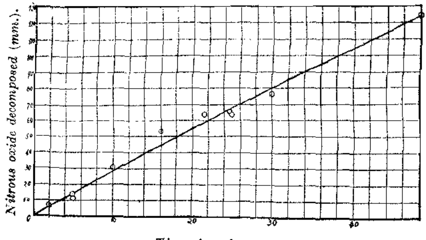
	Expt. 13(a).		Expt. 13(b).	
	1.	2.	1.	2.
Initial pressure (mm.)	115·0		115·4	
Time of exposure (mins.)	10		49·5	
Increase of pressure (1) (mm.)	3·0	3·0	7·0	10·6
Increase of pressure (2) (mm.)	1·4	1·5	5·56	5·3
N_2O decomposed (mm.)	5·9	(5·9)	21·8	(21·8)
Vol. permanent gas removed (c.c.)	0·54		1·91	
Vol. absorbed in pyrogallol (c.c.)	0·01		0·04	
Corresponding pressure of N_2	4·3	4·4	15·6	15·9
Corresponding pressure of O_2	0·1		0·3	

Col. 1 gives the actual experimental figures. Col. 2 gives the pressures which would have been observed had all the nitrous oxide

which disappeared decomposed according to the equation $4N_2O =$ $2NO_2 + 3N_2$. Two values are given for the increase of pressu due to decomposition. The first was measured immediately aft the exposure. The second was obtained after condensation of th gases in the liquid-air trap, evaporation, and keeping for some tim The difference is due to the fact that during a short exposure th nitrogen peroxide is not present as such, but as an equivalent mixtu of nitric oxide and oxygen. The combination of these two gases i slow at the extremely low partial pressures prevailing, and, accordin to Norrish (J., 1927, 761), nitrogen peroxide tends to decompos into nitric oxide and oxygen in ultra-violet light.

Fig. 3 shows the result of an experiment at 400 mm. pressure i which the time of exposure was varied. The curve is almos

FIG. 3.



straight, there being no falling off in the rate of decomposition tha cannot be accounted for by the lessened partial pressure of nitrou oxide present. There is no induction period. Similar experiment with vessel B showed a greater decrease of velocity with time, du to the screening effect of traces of nitrogen peroxide, formed by th slow combination of nitric oxide and oxygen, which took effect i the longer light-path in this vessel. In an experiment in which th combination of nitric oxide and oxygen was prevented by drying th apparatus and gas with special care, a high value was again obtained

The results of experiments at 100 mm. and 600 mm. pressure i vessel A, and at 100 mm. pressure and 0° and 15° in vessel B, ar in Table II. They are similar to that described above.

The results of experiments in which the pressure was varied and the time of exposure kept constant are in Table III. The values are plotted as circles in Fig. 4.

Table II.

Expt. 6. Vessel A. Initial pressure, 100 mm. Temp., 40°.

Time (mins.)	5	5	10	10	13	15	20	25	25·75	26	40
N_2O * (mm.)	*0·6*	*8·6*	*15·1*	*13·3*	*18·5*	*26·6*	*21·0*	*35·1*	*31·3*	*27·5*	*41·6*
N_2 (mm.) ...	13·5	13·9	11·6	—	14·3	21·6	—	32·1	28·1	—	39·2
NO_2 (mm.)	5·7	5·3	7·6	—	9·2	10·7	—	18·3	17·2	—	23·7
O_2 (mm.) ...	1·6	2·0	0·1	—	?	1·8	—	1·5	?	—	1·2

* The figures for N_2O denote the amount decomposed.

Expt. 7. Vessel A. Initial pressure, 600 mm. Temp., 40°.

Time (mins.) ...	5	10	12	13·5	20	25	27
N_2O (mm.)	18·1	29·6	32·4	40·3	59·8	61·9	76
N_2 (mm.)	14·1	23·3	29·2	30·8	50·2	59·2	55·8
NO_2 (mm.)	8·2	12·8	14·5	19·1	28·9	29·2	27·7
O_2 (mm.)	0·6	1·34	2·5	0·5	2·3	3·1	4·77

Expt. 8. Vessel B. Initial pressure, 100 mm. Temp., 15°.

Time (mins.) ...	7·3	8	10	12·5	12·7	18·25	21	34	66·5
N_2O (mm.)	4·3	3·8	5·1	6·4	6·3	8·2	8·6	12·1	16·4
N_2 (mm.)	3·2	2·8	4·4	4·8	4·6	6·15	6·3	9·1	12·3
O_2 (mm.)	?	0·0	0·1	0·0	0·1	?	0·1	0·0	0·2

Expt. 9. Vessel B. Initial pressure, 100 mm. Temp., 0°.

Time (mins.)	9	19	27·8
N_2O (mm.)	4·0	6·14	8·0
N_2 (mm.)	2·9	4·5	5·2
O_2 (mm.).............................	0·1	0·1	0·2

Fig. 4.

Nitrous oxide.

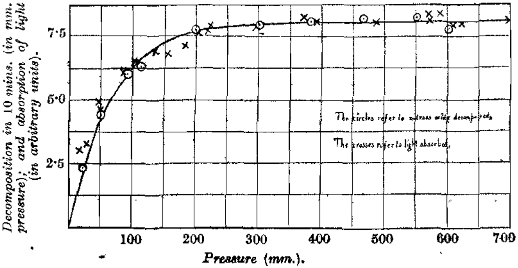


Table III.

Expt. 13. Vessel B. Decomposition in 10 minutes at 15°.

Initial press. (mm.)	21·3	49·7	91·1	115·0	200·8
N_2O decomposed (mm.) ...	2·3	4·4	6·0	6·3	7·75
Initial press. (mm.)	301·3	383·3	466·9	553·0	607·0
N_2O decomposed (mm.) ...	7·96	8·08	8·18	8·28	7·81

It was ascertained that the quantity of nitrogen peroxide formed in 10 minutes was negligible, and the values therefore give the true initial rate of decomposition.

The crosses in Fig. 4 show the absorption of light by nitrous oxide. This was measured by means of the thermopile, which received the light after it had passed through the vessel. The ordinates represent the difference between the deflexion of a Moll galvanometer when the light was allowed to pass through the evacuated vessel on to the thermopile, and that observed when the vessel was filled with a quantity of nitrous oxide. The abscissæ represent the pressure of nitrous oxide, as before. The observed deflexions were multiplied by a constant factor so chosen that one of the points (486 mm.) fell on the curve representing the rate of decomposition. It will be seen that the other points also fall on this curve, showing that the rate of decomposition, in the initial stages at least, is proportional to the amount of light absorbed.

That this absorption of light is represented quantitatively by Beer's law, *i.e.*,

$$\text{light absorbed} = \text{incident light} \times (1 - e^{-acd}) \quad . \quad . \quad . \quad (1)$$

(where a is the absorption coefficient, c the concentration, and d the length of the reaction vessel), is shown by the continuous line in Fig. 4, which is obtained by solving this equation for $c = 200$ mm. and $c = 600$ mm., two values of c being necessary in the absence of a direct measurement of the effective incident light.

The amount of light absorhed, as above measured, has been related to the decomposition occurring in unit time, thus giving the value of the quantum efficiency of the decomposition. First, the energy falling on 1 sq. cm. at 1 m. from a standard lamp in a certain position was determined by measuring the rate of rise of temperature on illumination of a metal disc which formed one junction of a thermocouple (compare Denning, *Phil. Mag.*, 1905, **10**, 270), and from this, the energy required to fall on the thermopile in order to give unit deflexion of the galvanometer was easily obtained. The value $2{\cdot}31 \times 10^{-4}$ cal. per sec. per cm. deflexion was found as a mean of about 12 determinations in each series, the maximum difference between any two experiments in either being 4%. This was multiplied by the deflexion caused by the presence in the apparatus of a given pressure of gas, so that the energy absorbed by that gas in 1 sec., and hence in 10 minutes, was obtained. This and the corresponding amount of decomposition were substituted in the formula

$$\gamma = (28470/\lambda) \times (\text{mols. decomposed/cals. absorbed}),$$

where γ is the quantum efficiency and λ the wave-length of active

light in microns. Actually, the light used was not monochromatic; but it was confined principally to the three lines at 1860 Å., 1930 Å., and 1990 Å. to which Pflüger (*Ann. Physik*, 1904, **13**, 890) assigns the relative intensities 173, 58, and 50, respectively. On the assumption, therefore, that the absorption is constant throughout this range, and that the activity of each line is proportional to its intensity, the effect would be equal to that of one line at 1900 Å. ($0{\cdot}19\mu$) with the same total intensity, and this value was substituted for λ in the above equation. When a correction of 5% for the reflexion and scattering of light by the fluorite plates had been applied, the value of γ was found to be $3{\cdot}9 \pm 0{\cdot}2$ mols. decomposed per quantum absorbed.

Temperature Coefficient.—It is of great importance, in studying the mechanism of any reaction, to find the temperature coefficient of the process; but, in the case of photochemical reactions, it is useless merely to state the value of such a coefficient, without indicating what factor is altering, for it may be due to a change either in the quantum efficiency or in the absorption coefficient. As already pointed ont, the rate of decomposition is proportional to the light absorbed at any temperature, and therefore

$$\text{rate} = KI(1 - e^{-acd}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where I is the intensity of the incident light and K is a constant. The value of this constant will depend on the quantum efficiency of the process, and it is necessary to find whether it is this or the value of a which changes with temperature.

If it can be assumed that a is independent of temperature, then it is merely necessary to compare the rates of reaction at the same concentration and different temperatures in order to obtain the temperature coefficient. If, however, a alters with temperature, the observed "temperature coefficient" will vary according to the pressure of gas under observation, for the rate of reaction is proportional to a at very low concentrations, and is independent of a when the pressure is sufficiently high to ensure that all the incident light is absorbed at the lowest temperature at which measurements are made. If K is constant, however, the variation of a with temperature can be found by comparing the pressures at which equal rates of reaction take place, for in this case the rates are equal when the product ac is the same in the experiments under comparison. Expt. 9 has therefore been compared with Expt. 8 (Table II) to give a value for the temperature coefficient on the assumption that a is constant, and with Expt. 13 (Table III) to give a value on the assumption that K is constant. These values are 1·24 and 1·49 respectively for a 10° rise.

It has been possible to show more particularly the variation of the two constants by correlating experiments in vessel A with experiments in vessel B, a process which, however, involved certain approximations. The constants used in drawing the curve in Fig. 4, referring to vessel *B* at 15°, were: $KI = 8{\cdot}1$, $a = 1{\cdot}04 \times 10^{-3}$. Four experimental points giving the amount of reaction in 10 minutes in vessel A at 40° at different pressures were plotted, and equation (2) was solved with these values. The constants of this equation were: $KI = 29{\cdot}5$, $a = 2{\cdot}47 \times 10^{-3}$, the latter depending on a calculation of the effective value of d, as the average of all possible rays of light from the source through the vessel. The ratio of the values of a in the two series, reduced for a 10° rise, is 1·44. This approaches as near as could be expected to the value of 1·49 found between 0° and 15° on the assumption that K was constant. The ratio of the values of K depends on the ratio of the incident light. The latter was calculated approximately, allowance being made for the light reflected and absorbed by the quartz vessel. The ratio of the values of K worked out at $0{\cdot}95 \pm 0{\cdot}1$ for a 10° rise. The quantum efficiency, therefore, does not alter appreciably with temperature, which only affects the amount of light absorbed.

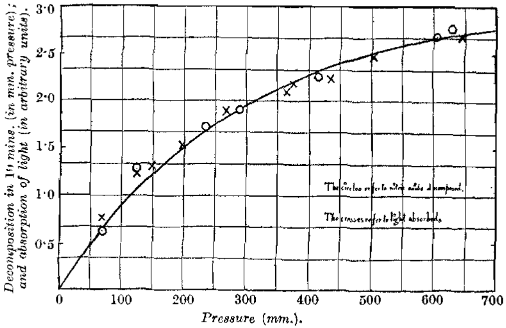
Results with Nitric Oxide.

This gas was less fully studied than nitrous oxide, which was the main object of research. Analyses showed that the reaction took place in two ways, one yielding nitrogen and oxygen, and the other nitrous oxide. The volume of nitrous oxide was only 10% of that of the nitrogen formed. In the majority of the experiments the nitrous oxide was present in too small a quantity to be estimated accurately, but there did not appear to be any considerable change in the proportion under the conditions studied, which were similar to those already described. The main experiments were directed towards determining the quantum efficiency, the rate of reaction and absorption of light at various pressures being also measured. The circles in Fig. 5 show the decomposition in 10 minutes (in mm. pressure) and the crosses show the light absorbed, reduced to the same scale. As in Fig. 4, the line is drawn as a solution of equation (2). The constants of this equation were: $KI = 3{\cdot}02$, $a = 2{\cdot}8 \times 10^{-4}$, so that the rate of reaction was lower than with nitrous oxide. The same wave-lengths of light were absorbed by nitric and by nitrous oxide, as was shown by the fact that both curves tended to the same maximum when light units (instead of mm. decomposition) were plotted as ordinates (compare also Leifson, *loc. cit.*). When this was again taken as 1900 Å., the quantum efficiency worked out at 1·45 mols. per quantum. That figure, however, is double the

real value, for, in the major reaction at least, every atom of oxygen produced united with a molecule of nitric oxide, and thus two molecules of the latter substance disappeared for every one which actually decomposed. The real efficiency is therefore about 0·75.

FIG. 5.

Nitric oxide.



The Mechanism of the Changes.

We have seen that nitrous oxide decomposes in light according to the equation

$$4N_2O = 2NO + O_2 + 3N_2 \quad . \quad . \quad . \quad . \quad (3)$$

the proportions of the products remaining constant over a considerable range of conditions, and a very small proportion of oxygen being always found over and above that necessary to satisfy the equation. The quantum efficiency is 3·9, a figure which does not alter appreciably between 0° and 40°. The absorption of light, however, has a temperature coefficient of 1·47.

It has also been shown that nitric oxide decomposes in two ways, according to the equations

$$2NO = N_2 + O_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$3NO = N_2O + NO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The proportion of the two reactions taking place was found to be about 90% of (4) and 10% of (5), a ratio which did not alter appreciably with the conditions of experiment, though comparatively small changes may have escaped observation. The quantum

efficiency is about 0·75, and the absorption coefficient is less than that of nitrous oxide.

There are three general mechanisms by which nitrous oxide might decompose according to equation (3): (*a*) One of the substances on the right-hand side might be an intermediate product in the formation of the others; (*b*) two concurrent reactions might take place; or (*c*) an *intermediate* product might be formed, which does not appear in the final products. Hypothesis (*a*) is disproved by the constancy of the products, and also by the fact that the known rates of decomposition of nitric oxide and of union of nitrogen and oxygen are far too slow to account for any measurable amount of such secondary reaction taking place. Mechanism (*b*), expressed as the equations

$$\left.\begin{aligned} N_2O + N_2O' &= 2N_2 + O_2 \\ N_2O + N_2O' &= 2NO + N_2 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

(where N_2O' represents an activated molecule) is possible. The different courses of reaction could be explained by a difference in the activation of the molecule, either of two electrons being capable of elevation to a higher Bohr state, or by a different orientation at the moment of collision. In that event, however, the almost exact equivalence of nitric oxide and oxygen produced could only be fortuitous, and one would expect only 2 molecules to be decomposed per quantum instead of nearly 4, as found. The fact that the quantum efficiency did not alter with temperature or pressure is strong evidence that every activated molecule reacts, involving the decomposition of 3 other molecules. The length of an " indefinite " chain mechanism would be altered by an increase in the average energy of the system or in collision frequency. There remains the third mechanism, (*c*). The formation of nitrogen peroxide as an intermediary may be ruled out. Norrish (*loc. cit.*) found that the efficiency at 3650 Å. was not more than 0·03 molecule per quantum. To obtain the observed results, this would have to rise to a very high value (say, 20) at 1900 Å., and the very unlikely event of a four-fold collision would have to be assumed.

The following series of equations, however, satisfies all the necessary conditions :

$$\left.\begin{aligned} &(a) \quad N_2O + h\nu = N_2O' \\ &(b) \quad N_2O' + N_2O = O_2 + N_2 + 2N \\ &(c) \quad 2(N + N_2O = NO + N_2) \end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

The only one of these open to question is (*b*). Such a reaction between normal molecules would be endothermic to the extent of about 120,000 cals. per mol. The energy associated with a quantum

of wave-length 1900 Å. is, however, 150,000 cals. per mol. The equation is, therefore, quite plausible thermally. The reaction may be pictured as follows. An active molecule comes into collision with a normal one, and a large amount of energy becomes available for redistribution. The first result is that two nitrogen atoms are ejected, and simultaneously the less energetic break-up of the complex N_2O_2 into nitrogen and oxygen occurs. The liberated nitrogen atoms will eventually come into collision with nitrous oxide molecules, and reaction (*c*) takes place. It is probable that a few of the nitrogen atoms combine with each other, for the observed rate of photochemical decomposition of nitric oxide is scarcely sufficient to account for even the small excess of oxygen found by analysis.

It is instructive to compare the photochemical decomposition of nitrous oxide with the other known decompositions. Both in the decomposition by α-rays (Wourtzel, *loc. cit.*) and in that by the silent electric discharge (Joshi, *loc. cit.*), reactions summarised by the equation $4N_2O = 2NO_2 + 3N_2$ take place. It is attractive to assume that in both these cases the mechanism outlined above operates. In the thermal reaction at comparatively low temperatures (Hinshelwood and Burk, *loc. cit.*) nitrogen and oxygen are the chief products. At higher temperatures, however, nitric oxide is produced in increasing quantities till a maximum is reached (Briner, Meiner, and Rothen, *loc. cit.*), when the rate of formation of this substance is balanced by its decomposition. As much as 25% of nitric oxide was found in the products. It is possible that in this case the higher temperature provides the energy necessary for reaction 7 (*b*) to take place also.

The mechanism of the decomposition of nitric oxide is much less clear. The quantum efficiency is low, and its variation with temperature is not known. If, as is probable, it increases with temperature, the maximum to which it tends is doubtful. On lines similar to those given above, a possible mechanism would appear to be the simultaneous reactions $NO + NO' = N_2 + O_2$ and $NO + NO' = N_2O + O$, followed by $NO + O = NO_2$. It should be noticed, however, that nitric oxide seems to be peculiarly liable to multimolecular reactions (compare Hinshelwood and Green, J., 1926, 730), pointing to some stability in the complex formed by the collision of two molecules. Should such a complex be struck by an active molecule, the reaction $(2NO) + NO' = N_2O + NO_2$ would take place, while the bimolecular reaction might give only nitrogen and oxygen. Briner and Boubnoff (*loc. cit.*) studied the thermal decomposition at high pressures. The reaction was of the third or fourth order, and nitrous oxide was mainly produced, some

nitrogen being found. At high temperatures and ordinary pressures, Briner, Meiner, and Rothen (*loc. cit.*) found no nitrous oxide in the products of decomposition. A survey of the behaviour of nitric oxide under different modes of decomposition given by Briner and Boubnoff seems to show that the proportion of nitrogen generally increases with temperature. This might be due to the increase of energy of collision, or to the shortened life-period of the complex (2NO). The question requires further investigation.

Summary.

The decomposition of nitrous and nitric oxides in light of wave-length *1860—1990* Å. has been studied.

Nitrous oxide decomposes according to the general equation $4N_2O = 2NO + O_2 + 3N_2$, the proportions of the products being constant over a considerable range of conditions. The quantum efficiency is $3{\cdot}9 \pm 0{\cdot}2$, and does not vary appreciably with temperature between 0° and 40°, nor with pressures up to about 1 atmosphere. The absorption coefficient increases $1{\cdot}47 \pm 0{\cdot}05$ times for a 10° rise of temperature. A mechanism has been suggested for the decomposition which may be applicable to decompositions by other agencies.

Nitric oxide decomposes in two ways, according to the equations $2NO = N_2 + O_2$ and $3NO = N_2O + NO_2$, the first reaction constituting about 90% of the whole. The quantum efficiency is $0{\cdot}73 \pm 0{\cdot}05$. Two possible mechanisms are suggested. There is insufficient evidence, however, to warrant a decision.

Beer's absorption law holds strictly for both gases. Nitrous oxide, however, absorbs light several times more strongly than nitric oxide.

In conclusion, the author wishes to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant, to Messrs. Brunner Mond and Co. for a grant which provided much of the apparatus, and especially to Professor F. G. Donnan for suggesting the research, for the kindly interest with which he followed its progress, and for his helpful advice.

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II.—*The Pressures produced on Inflammation of Mixtures of* (a) *Carbon Monoxide and Air, and* (b) *Hydrogen and Air in a Closed Spherical Vessel.*

By GEORGE BARTON MAXWELL and RICHARD VERNON WHEELER.

RECORDS of the rate of development of pressure in mixtures with air of carbon monoxide and hydrogen, ignited at the centre of a closed spherical vessel, were given in J., 1927, 297. In the present paper, the magnitudes of the pressures are recorded, and deductions are drawn from them as to the dissociation of carbon dioxide and the specific heat of steam. The general character of the apparatus used is described in J., 1918, **113**, 844. The sphere was of bronze, of 4 litres capacity, with its interior highly polished.

The Dissociation of Carbon Dioxide.

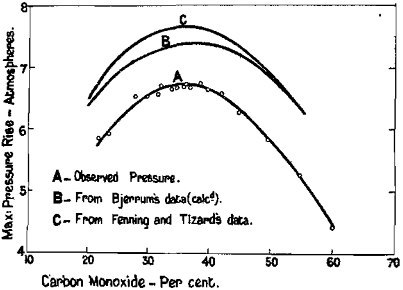
As a result of experiments on the inflammation of mixtures of air with the paraffins (J., 1927, 2069), we called in question Nernst and Bjerrum's values for the dissociation of carbon dioxide. Fenning and Tizard (*Proc. Roy. Soc.*, 1927, *A*, **115**, 318) also have questioned those values, and their experiments indicate that at high temperatures the dissociation has been considerably over-estimated. Fenning and Tizard's method of determining the equilibrium constant of the system $2CO_2 \rightleftharpoons 2CO + O_2$ at different temperatures was to explode carbon monoxide in various proportions with different "atmospheres," ranging from air to pure oxygen, thus finding the "maximum-pressure mixture" for each atmosphere experimentally. This method demands highly accurate relative pressure measurements, since it is not easy to decide which mixture develops the highest pressure on explosion. It was assumed in Fenning and Tizard's calculations that heat losses for mixtures on either side of the "maximum-pressure mixture" would not differ much. This assumption was known to be incorrect (owing to the shape of their explosion vessel) when the times of explosion were widely different, and a correction, in which the heat loss was regarded as proportional to the time of explosion, was then applied.

In our experiments, the results of which are recorded in Table I, differences in heat losses due to conduction appear to have been negligible, for, on explosion of mixtures of the same composition when dried and undried, the pressures developed by the latter were slightly the lower (owing to their moisture contents) despite the fact that their times of explosion were much the shorter. The

principal heat loss would be by radiation. This would be minimised by the polished interior of the explosion vessel.

The results for the dried mixtures recorded in Table I were obtained with a Petavel gauge, modified to record comparatively low pressures (up to 20 atm.), which had been calibrated by means of compressed air against a standard Bourdon gauge. The results for the undried mixtures were obtained partly with this gauge and partly with one of the moving-piston type (see J., 1918, **113**, 844), calibrated by means of a dead-weight oil ram.

Fig. 1.



Observed and calculated pressures in CO–Air Mixtures.

TABLE I.

The Explosion of Mixtures of Carbon Monoxide and Air.

(a) Mixtures dried by calcium chloride.		(b) Mixtures saturated with water-vapour at 15°. (i) Petavel gauge.		(ii) Piston gauge.	
% CO.	Max. press. rise (atm.).	% CO.	Max. press. rise (atm.).	% CO.	Max. press. rise (atm.).
19·40	4·83	21·60	5·83	29·90	6·53
24·90	6·29	23·50	5·93	32·00	6·71
30·55	6·61	27·95	6·53	33·40	6·69
33·10	6·74	31·10	6·56	33·70	6·65
40·00	6·70	36·65	6·67	34·40	6·67
45·80	6·17	39·50	6·62	35·40	6·70
49·65	5·80	44·90	6·29	35·90	6·71
		49·65	5·82	38·10	6·72
		54·75	5·29	42·00	6·58
		60·00	4·42		

The results in Table I (for the undried mixtures only, to ensure strict comparison) are shown graphically in Curve A, Fig. 1. From this curve, when plotted on a larger scale, it can be seen that the

"maximum-pressure mixture" of carbon monoxide and air contains 35·5% of carbon monoxide and develops a pressure of 6·72 atm. Using the same method of calculation as Fenning and Tizard, this result gives for the dissociation of carbon dioxide :

b.	a.	$x(=a/b)$.	P_e (atm. abs.).	T_e (° Abs.).	K_p.
3·79	0·283	0·075	7·72	2543	0·0135

The term b is the ratio nitrogen : oxygen in the atmosphere (air); it appears in the expression for the composition of the original mixture : $2(1 + a)CO + O_2 + bN_2$; P_e is the maximum explosion pressure and T_e the corresponding temperature; K_p is the required dissociation constant $P^2_{CO} \times P_{O_2}/P^2_{CO_2}$, where P_{CO}, P_{CO_2}, and P_{O_2} are the partial pressures at equilibrium of carbon monoxide, carbon dioxide, and oxygen.

Fenning and Tizard's value for K_p at 2543° K. is $1·66 \times 10^{-3}$, whilst Bjerrum's (*Z. physikal. Chem.*, 1912, **79**, 513) figure is $3·4 \times 10^{-3}$. Expressed as percentages, the corresponding values at 1 atm. and 2543° K. are : Fenning and Tizard, 14·9; Bjerrum, 23·4; Maxwell and Wheeler, 30·1. Our result thus does not support Fenning and Tizard's, nor our own suggestion that Bjerrum's dissociation values at high temperatures have been over-estimated. It is clear that the absolute values for the dissociation constants obtained by the method of "maximum-pressure mixtures" must be looked on with caution, even when the experimental work has been carried out with great care. In this connexion, it should be noted that in four out of the five series of experiments on which Fenning and Tizard based their calculations, the "maximum-pressure mixture" was deduced from but four trials. Our curve embodies the results of 19 duplicate experiments, in 10 of which the composition of the mixture lay within the range 30—40% carbon monoxide.

Perhaps a more useful test of the relative value of the dissociation constants as determined by the method of "maximum-pressure mixtures" is to use them for calculated pressures, for a range of mixtures, to compare with observed pressures. We have made such calculations (see Appendix) and give the results as curves in Fig. 1, B calculated from Bjerrum's data and C from Fenning and Tizard's. Curve C follows more closely than does Curve B the general form of the experimental curve (A), and from it the calculated and observed maximum-pressure mixtures are identical, whereas from Curve B the maximum-pressure mixture should contain about 38% of carbon monoxide.

The observed maximum pressure-rise (curve A) was 6·72 atm., whereas the calculated values are : Curve B, 7·38 atm.; and

Curve C, 7·65 atm. Inasmuch as our experimental method reduced heat losses during explosion to a minimum, these discrepancies appear excessive, and it must be pointed out that the estimation of dissociation constants from explosion experiments involves the assumption that chemical equilibrium has been attained in the system at the moment of maximum pressure. This assumption does not appear to be warranted in view of the evidence adduced by Ellis and Wheeler (J., 1927, 153) with regard to "after-burning" on explosion of mixtures of carbon monoxide and air.

In general, we suggest that Fenning and Tizard's values for the dissociation of carbon dioxide at different temperatures are, relatively, more consistent with the results of explosion experiments, such as those described in this paper, than are Bjerrum's; but that, if, as seems certain, combustion be incomplete at the moment of maximum pressure, the absolute magnitudes of those values cannot be accepted.

The Specific Heat of Steam.

The pressures (recorded by the Petavel gauge) developed on explosion of mixtures of hydrogen and air in a closed 4-litre sphere are given in Table II.

TABLE II.

The Explosion of Mixtures of Hydrogen and Air.

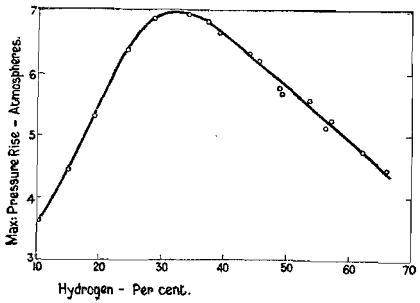
% H_2	Max. press. rise (atm.).	% H_2.	Max. press. rise (atm.).	% H_2.	Max press rise (atm.).
10·2	3·63	37·2	6·82	54·0	5·57
15·1	4·45	39·35	6·65	56·2	5·12
19·4	5·30	44·4	6·32	57·2	5·27
24·5	6·38	45·8	6·20	62·3	4·73
28·9	6·89	49·0	5·78	66·1	4·45
34·1	6·92	49·2	5·66		

From Fig. 2, which expresses these results graphically, it appears that the maximum pressure rise (6·98 atm.) would be obtained by a mixture containing 32·5% hydrogen, a displacement of 3% from the theoretical "complete combustion" mixture.

The disagreement amongst recent determinations of the specific heat of steam at high temperatures was commented on in our paper on the explosion of mixtures of air with the paraffins (*loc. cit.*), where it was suggested that the high values obtained by Womersley over the range 1500—2000° (*Proc. Roy. Soc.*, 1921, *A*, **100**, 483) might be nearer the truth than Bjerrum's. In order to estimate the mean values for the specific heat of steam at constant volume from the results of explosion experiments, it is necessary to know the composition of the products at the moment of maximum temperature. By the use of Fenning and Tizard's method of calculating

he dissociation of steam in the products of the maximum-pressure ydrogen–air mixture (32·5% hydrogen), it is found that the mean emperature is 2645° K. At that temperature $K_p = 0{\cdot}002$, equiva-ent to a dissociation of 15·9% at 1 atm. and 2645° K. The value iven by Bjerrum (*Z. Elektrochem.*, 1911, **17**, 731; 1912, **18**, 101) s 2·8%. This discrepancy accentuates the untrustworthiness of he "maximum-pressure mixture" method of determining dis-ociation constants. It also suggests that, under the conditions f explosion experiments, where there is a marked temperature radient from the centre to the walls of the explosion vessel at the

FIG. 2.



Hydrogen–Air Mixtures.

aoment when the explosion is completed, an accurate estimation f the composition of the gases at that moment cannot be made rom Bjerrum's figures. For this reason, we have chosen, for alculations of the specific heat of steam, mixtures containing suffi-ient excess of hydrogen to repress the dissociation of steam.

As an example, a calculation based on the pressure produced on xplosion of a mixture containing 50% of hydrogen is given in etail. From Fig. 2 the pressure rise with this mixture is found o be 5·80 atm., corresponding with a corrected value (see *J.*, 927, 2069) of 5·9 atm. The initial mixture, saturated with vater vapour at 15° and 1 atm., contained, per unit vol., H_2, ·4915; O_2, 0·1028; N_2, 0·3887; H_2O, 0·0170. On the assumption hat there is complete combustion (and no dissociation) the products t the moment of maximum pressure would contain: H_2, 0·2859; O_2, nil; N_2, 0·3887; H_2O, 0·2226. The "molecular ratio" (see

Appendix) is 0·8972, from which the mean temperature at the moment of maximum pressure, T_e, is $288 \times 6·9/0·8972 = 2215°$ K., or 1942° C.

In order to calculate the mean specific heat of steam at constant volume over the range 15—1950° from these data, the mean specific heats of hydrogen and nitrogen over the same range must be known. We have used the values recorded by Partington and Shilling ("The Specific Heats of Gases," London, 1924), which are based on a number of consistent determinations. We have also taken Nernst's figure, 57,500 cals. per g.-mol. at constant volume, for the lower calorific value of hydrogen. Over the range 0—1950°, C_v for H_2 and $N_2 = 5·525$. If C be the mean specific heat of steam over the same range, $0·2226C + (5·525 \times 0·6746) = 0·2056 \times 57{,}500/(2215 - 288)$; whence $C = 10·8$ cal. per g.-mol.

The results of calculations based on the pressure rise on explosion of four mixtures rich in hydrogen (containing 66·1, 57·2, 50·0, and 45·0%) are given in Table III.

TABLE III.

Mean Specific Heat of Steam at Constant Volume (cals. per g.-mol.).

	Partington and Shilling.	Womersley.	Maxwell and Wheeler.
$t°$.	$0—t°$.	$100—t°$.	$15—t°$.
1400	7·45	8·35	10·7
1750	8·1	10·2	10·6
1950	8·5	11·4	10·8
2120	8·9	11·7	10·6

Our results thus approximate closely to Womersley's, although they suggest that the specific heat of steam does not increase appreciably over the range 1400—2120°.

NOTE.—There is a possible source of error in Womersley's paper which has been brought to our notice by Professor H. B. Dixon.

Womersley gives as the nett calorific value of hydrogen (hydrogen to steam) 67,840 cals. per g.-mol. The authority is given as Ostwald's "Lehrbuch der Allgemeinen Chemie."

Of course Ostwald gives this figure for the gross value (hydrogen to water). Since Womersley does not give the analyses on which his calculations were based, it is not possible to determine from his paper whether the error affects his results or is only an error of statement.

Appendix.

The calculations from which Curves B and C of Fig. 1 were constructed are given in Table IV. The method of calculation is described in J., 1927, 2069.

TABLE IV.

Mixtures of Carbon Monoxide and Air.

Calculated maximum temperatures and pressures.

(*a*) From Bjerrum's dissociation values.

CO, %.	Products of combustion (% by vol.) at moment of max. temp. CO_2.	CO.	O_2.	N_2.	Molecular ratio.*	Max. temp.	Pressure rise (atm.).
20·0	21·3	0·8	7·9	70·0	0·904	2080°	6·38
25·0	24·4	3·6	5·6	66·4	0·893	2310	7·01
30·0	25·8	8·1	3·6	62·5	0·885	2415	7·26
35·0	26·4	13·2	2·2	58·2	$0{\cdot}883_5$	2455	7·36
38·5	26·4	17·2	1·3	55·1	0·883	2460	7·38
45·0	25·3	25·4	0·3	49·0	0·888	2380	7·17
55·0	20·8	39·9	Trace	39·3	0·906	2045	6·29
			(*b*) From Fenning and Tizard's data.				
20·0	21·7	0·5	7·7	70·1	0·902	2115°	6·48
25·0	25·2	3·0	5·1	66·7	0·888	2385	7·19
30·0	27·2	6·9	3·0	62·9	0·880	2515	7·52
35·0	27·9	12·0	1·6	58·5	0·878	2565	7·65
38·5	27·7	16·1	0·8	55·4	$0{\cdot}878_5$	2555	7·62
45·0	25·8	25·0	0·1	49·1	0·886	2415	7·28
55·0	20·8	39·9	Trace	39·3	0·906	2045	6·29

* The ratio of the number of molecules present at the moment of maximum ·mperature to the initial number.

Some of the experiments described in this paper were carried out ı connexion with a research for the Safety in Mines Research ·oard, to whom our thanks are due for permission to use the results. /e also wish to thank Mr. E. M. Guénault, M.Sc., for assistance ith the experimental work.

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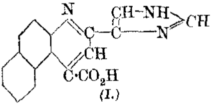
III.—*Glyoxaline-4(5)-formaldehyde.*

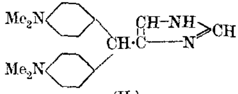
By WILFRID HUBBALL and FRANK LEE PYMAN.

HIS research had the double object of studying the reactions of ·yoxalinealdehydes, especially in comparison with benzaldehyde, nd of determining the orienting effect of the carbonyl group in ıe methylation of these and related compounds. Glyoxaline- ·5)-formaldehyde had been shown previously to yield a cyano- ydrin and a phenylhydrazone (Pyman, J., 1916, **109**, 186); the *·til, oxime, semicarbazone* and *sodium bisulphite compound* are ow described. It had been condensed previously with malonic ·id (Barger and Dakin, *Biochem. J.*, 1916, **10**, 376) and with ippuric acid, but attempts to convert it into glyoxaline-4(5)- ·rylic acid by Perkin's method were unsuccessful (Pyman, *loc.*

cit.). Renewed attempts to effect its condensation with othe compounds containing reactive methylene groups have been ur satisfactory; no condensation product was obtained with acetoni whilst condensation with acetophenone or ethyl acetate (by Claisen' method) gave very poor yields of the desired products. It con densed readily, however, with pyruvic acid and β-naphthylamine yielding 2-[*glyoxalinyl*-4(5)]-β-*naphthacinchoninic acid* (I), and wit dimethylaniline, yielding pp′-*tetramethyldiaminodiphenyl*[*glyoxaliny* 4(5)-]*methane* (II), which gave a dye closely resembling malachite green on oxidation.

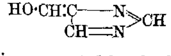


(I.)



(II.)

Glyoxaline-4(5)-formaldehyde is not oxidised by air or ammoniaca silver nitrate. It does not undergo Cannizzaro's reaction, nc react with ammonia to give a compound of the hydrobenzamid type, being recovered unchanged in each case. It does not restoı the colour to magenta decolorised by sulphurous acid, and doe not undergo acetalisation by Fischer and Giebe's method (*Ber* 1897, **30**, 3053). Its aldehyde group does not react with magnesiuı methyl iodide. Attempts to convert it into a benzoin-like con pound by means of potassium cyanide, and to condense it wit nitromethane by means of alcoholic potassium hydroxide, resulte in uninviting resinous compounds.* In short, it does not sho the properties typical of benzaldehyde which are shared by th aldehydes of many non-acidic heterocyclic compounds, such a furfuraldehyde, thiophen-α-aldehyde, and pyridine-α-aldehyde, bu resembles the acidic *o*- and *p*-hydroxybenzaldehydes and pyrrole α-aldehyde, which also fail to undergo many of the reactions chaı acteristic of benzaldehyde (compare Pauly and von Buttlar, *Annale* 1911, **383**, 230). In common with these substances, its behavioı may be attributed either to the presence of an acidic group (·O] or :NH), or to stability in the tautomeric hydroxymethylene forn



(III.)

which in this case is represented by the formula (III), and it wa to be expected that its *N*-methyl derivatives would show th

* Details of these negative experiments are not recorded below, but wi be found in the M.Sc. Tech. thesis of W. Hubball, University of Manchéste 1922.

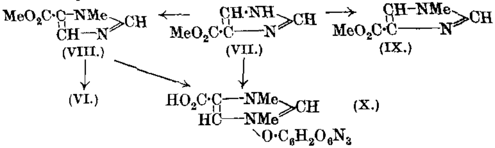
typical reactions of benzaldehyde, just as anisaldehyde, for example, undergoes the Cannizzaro reaction, although *p*-hydroxybenzaldehyde fails to do so. For this reason and others the preparation of *N*-methylated glyoxalineformaldehydes was attempted by the methylation of glyoxalineformaldehyde, and 1-methylglyoxaline-5-formaldehyde was isolated but in so poor a yield that its properties could not be investigated fully. It proved, however, to undergo the Cannizzaro reaction normally, yielding the corresponding acid and alcohol (as did also 1 : 4-dimethylglyoxaline-5-formaldehyde, XIV).

The methylation of glyoxalineformaldehyde was of interest also from another point of view. It has been shown previously (Hazeldine, Pyman, and Winchester, J., 1924, **125**, 1431; Balaban and Pyman, *ibid.*, p. 1564) that methylation of 4(5)-nitroglyoxaline and of 4(5)-bromoglyoxaline by methyl salts yields mainly 5-nitro-(or bromo)-1-methylglyoxaline with little 4-nitro(or bromo)-1-methylglyoxaline, and it was to be expected that the carbonyl group of glyoxaline-4(5)-formaldehyde would have a directive effect similar to that of the nitro-group, leading to the predominant formation of 1-methylglyoxaline-5-formaldehyde. Methylation of glyoxaline-4(5)-formaldehyde, however, proceeded very unsatisfactorily from the point of view of the formation of its monomethyl derivatives, for in several experiments under various conditions a considerable proportion was recovered unchanged, this indicating the formation of a corresponding quantity of the dimethylated quaternary salt. Consequently only poor yields of 1-*methylglyoxaline-5-formaldehyde* (IV) were obtained, and the isomeric 1-methylglyoxaline-4-formaldehyde was not isolated. The constitution of the base (IV) was proved through its reduction by hydriodic acid and phosphorus to 1 : 5-dimethylglyoxaline (V). On oxidation, it gave 1-*methylglyoxaline-5-carboxylic acid* (VI).

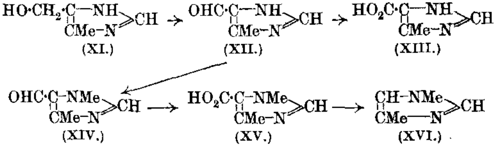
(VI.) (IV.) (V.)

The directive influence of the carbonyl group was studied further in the methylation of methyl glyoxaline-4(5)-carboxylate (VII) and 4(5)-methylglyoxaline-5(4)-formaldehyde. Methylation of the ester gave a fair yield (about 37%) of *methyl* 1-*methylglyoxaline-5-carboxylate* (VIII) together with a very small quantity (0·9%) of *methyl* 1-*methylglyoxaline-4-carboxylate* (IX), some unchanged material, and the dimethylated quaternary base isolated as 4(5)-*carboxy*-1 : 3-*dimethylglyoxalinium picrate* (X). The constitution of (VIII) was determined by hydrolysis, the acid (VI) being obtained, whilst the constitution of (X) was determined through its formation

by methylation and hydrolysis of (VIII), combined with the results of methoxyl and *N*-methyl determinations.



4(5)-*Methylglyoxaline*-5(4)-*formaldehyde* (XII) was prepared by the oxidation of 4(5)-methyl-5(4)-hydroxymethylglyoxaline (XI) by means of nitric acid; 4(5)-methylglyoxaline-5(4)-carboxylic acid (XIII), which had been prepared previously in other ways by Gerngross (*Ber.*, 1912, **45**, 509), was obtained as a by-product. The aldehyde has not been described previously, although Gerngross (*loc. cit.*) prepared its anil from 4(5)-methylglyoxaline-5(4)-glyoxylic acid.



Methylation of 4(5)-methylglyoxaline-5(4)-formaldehyde proceeded more smoothly than that of the lower homologue, and 1 : 4-*dimethylglyoxaline*-5-*formaldehyde* (XIV) was obtained in fair yield, but none of the isomeric 1 : 5-dimethyl-4-formaldehyde could be isolated. The constitution of (XIV) was determined (1) by oxidising it to the corresponding acid, 1 : 4-*dimethylglyoxaline*-5-*carboxylic acid* (XV), and decarboxylating this, 1 : 4-dimethylglyoxaline (XVI) being formed, and (2) through its formation by the oxidation of 1 : 4-dimethyl-5-hydroxymethylglyoxaline (Grindley and Pyman, J., 1927, 3128). The results of methylating glyoxaline-4(5)-formaldehyde, its 5(4)-methyl homologue, and methyl glyoxaline-4(5)-carboxylate show clearly that the carbonyl group, like the nitro-group and bromine atom, leads to the predominant formation of 5 : 1-methyl derivatives.

EXPERIMENTAL.

Glyoxaline-4(5)-formaldehyde has *M* 96 (by Rast's method) (Calc. for $C_4H_4ON_2$: *M*, 96). The *nitrate* crystallises from water

in colourless, elongated plates, m. p. 165° (corr.) (Found: C, 30·1; H, 3·2; N, 26·5. $C_4H_4ON_2,HNO_3$ requires C, 30·2; H, 3·1; N, 26·4%). The *hydrochloride* crystallises from water in colourless plates which are hygroscopic and after drying over sulphuric acid melt at 169—170° (corr.) (Found in dried salt: Cl, 26·6. $C_4H_4ON_2,HCl$ requires Cl, 26·8%).

Glyoxaline-4(5)-methylideneaniline.—The aldehyde (1 g.) dissolved in aniline (1·5 g.), but the clear liquid soon solidified. The *anil* crystallised from water in long, stout, colourless needles, m. p. 142—143° (corr.) (Found: C, 70·0; H, 5·5; N, 24·3. $C_{10}H_9N_3$ requires C, 70·2; H, 5·3; N, 24·6%). It is sparingly soluble in cold water, but readily soluble in alcohol or acetone.

Glyoxaline-4(5)-formaldoxime.—The aldehyde (0·5 g.), hydroxylamine hydrochloride (0·35 g.), and sodium carbonate (0·25 g.) gave on keeping in aqueous solution 0·53 g. of the *oxime*, m. p. 181—183°. After recrystallisation from alcohol, it formed colourless prisms, m. p. 183—184° (corr.) (Found: C, 43·0; H, 4·6; N, 37·7. $C_4H_5ON_3$ requires C, 43·2; H, 4·5; N, 37·8%). It is very sparingly soluble in cold water, alcohol, or acetone.

Glyoxaline-4(5)-formaldehyde semicarbazone, prepared from the aldehyde, semicarbazide hydrochloride, and sodium acetate in 75% yield, crystallised from water in colourless needles containing $1H_2O$, m. p. (after drying) 223—224° (corr.) (Found in air-dried substance: loss at 120°, 11·2. $C_5H_7ON_5,H_2O$ requires H_2O, 10·5%. Found in substance dried at 110°: C, 39·4; H, 4·4; N, 45·9. $C_5H_7ON_5$ requires C, 39·2; H, 4·6; N, 45·8%). It is fairly readily soluble in hot water, but sparingly soluble in cold water or hot alcohol.

The *glyoxaline-4(5)-formaldehyde-sodium bisulphite compound* crystallised from water in colourless plates, which darkened on heating to 200° (Found in air-dried material: Na, 11·1. $C_4H_5O_3N_2SNa$ requires Na, 11·5%). It is very readily soluble in hot water, moderately soluble in cold water, and almost insoluble in alcohol.

Glyoxaline-4(5)-formaldehyde and Acetone.—An attempt to condense the aldehyde with acetone under the conditions employed by Claisen (*Ber.*, 1881, **14**, 2468) for the condensation of benzaldehyde with acetone was unsuccessful. After a mixture of glyoxalineformaldehyde (0·3 g.), acetone (0·3 c.c.), and 10% aqueous potassium hydroxide (3 c.c.) had been kept for several days, the aldehyde was recovered in 84% yield.

Glyoxaline-4(5)-formaldehyde and Acetophenone.—Dry hydrogen chloride was passed through a solution of glyoxaline-4(5)-formaldehyde (1 g.) and acetophenone (1·26 g.) in glacial acetic acid for 3 hours. The solution was heated at 100°, kept over-night,

and mixed with aqueous sodium carbonate; an oil (0·6 g.) the separated. This was converted into picrate and crystallise fractionally; it then gave the picrate of the unchanged aldehyd (0·5 g.; yield, 14·8%), and a second picrate (0·07 g., m. p. 201 [corr.]; yield, 3·2%), which crystallised from water in yello needles and gave fairly satisfactory analytical figures for glyoxaline 4(5)-methylideneacetophenone picrate (Found in air-dried salt C, 51·2; H, 2·9; N, 16·6. $C_{12}H_{10}ON_2,C_6H_3O_7N_3$ requires C, 50·6 H, 3·0; N, 16·4%).

Glyoxaline-4(5)-formaldehyde and Ethyl Acetate.—In an attemp to condense these substances by Claisen's method (*Ber.*, 1890, 23 976), glyoxalineformaldehyde (1 g.), ethyl acetate (5 c.c.), an sodium (0·25 g.) were mixed and kept, first at the ordinary ten perature and then on the water-bath. The product consisted c an ethyl acetate solution and a residue. The latter gave glyoxaline formaldehyde picrate in 40% yield, whilst the substance dissolve in the ethyl acetate solution gave with picric acid a salt which after repeated crystallisation from water, formed yellow needles amounted to 0·15 g. (yield, 5%), blackened and decomposed a 250° after sintering from 230°, and gave figures on analysis indicatin that it was the *picrate* of *ethyl urocanate* (ethyl glyoxaline-4(5) acrylate) (Found: C, 42·4; H, 3·7. $C_8H_{10}O_2N_2,C_6H_3O_7N_3$ require C, 42·5; H, 4·2%). Attempts to repeat the preparation of thi compound were unsuccessful.

2-[*Glyoxalinyl*-4(5)]-β-*naphthacinchoninic Acid* (I).—The aldehyd (1 g.), pyruvic acid (1 g.), and β-naphthylamine (1·5 g.) were boile in alcohol for 1 hour; the above acid (1·82 g.; yield, 62%) the separated. It crystallised from dilute acetic acid in very fine yellow needles, decomp. 300° (Found: C, 70·5; H, 3·8; N, 14·($C_{17}H_{11}O_2N_3$ requires C, 70·6; H, 3·8; N, 14·5%). It is sparingl soluble in hot dilute acetic acid and almost insoluble in cold dilut acetic acid.

pp′-*Tetramethyldiaminodiphenyl*[*glyoxalinyl*-4(5)-]*methane* (II).– The aldehyde (1 g.), dimethylaniline (2·5 g.), and concentrate hydrochloric acid (2 g.) were heated for 4 hours at 100°. Th viscous product was dissolved in water, basified with sodiu carbonate, and distilled with steam to remove unchanged dimethy aniline. After cooling, the aqueous solution was decanted, an the amorphous product which had separated on the sides of th distillation flask was crystallised from alcohol. Yield, 1·73 g. 52%. It was dissolved in alcohol and precipitated by ether; i then formed colourless clusters of needles, m. p. 190° (corr.), whic soon became green in the air (Found: C, 74·9; H, 7·5; N, 17·($C_{20}H_{24}N_4$ requires C, 75·0; H, 7·5; N, 17·5%). The *leuco*-bas

gave a clear, almost colourless solution in dilute hydrochloric acid.

Oxidation. The *leuco*-base (0·22 g.) was dissolved in water (100 c.c.) and very small quantities of hydrochloric and acetic acids, and lead dioxide paste (2 g.) was added gradually at 5° with constant shaking. After 5 minutes, sodium sulphate (0·25 g.) was added to the deep green solution, and lead sulphate was removed. The filtrate was mixed with ammonia; the colour base was then precipitated as a purple, crystalline powder (yield, 0·18 g.; 80%). It dissolves in acids to give deep green solutions, and dyes tanned cotton jade-green.

Methylation of Glyoxaline-4(5)-formaldehyde.—When glyoxaline-formaldehyde (1 g.) and methyl sulphate (1 c.c.) were mixed and warmed gently, a vigorous reaction took place. The product was dissolved in water, basified with sodium carbonate, and extracted with ether, crude 1-methylglyoxaline-5-formaldehyde (0·1 g.) being thus removed. It was converted into picrate and gave after crystallisation 0·2 g. of the pure salt (yield, 5·7%). From the alkaline mother-liquor glyoxalineformaldehyde was recovered as picrate in 44% yield.

Methylation of glyoxalineformaldehyde with either methyl iodide or methyl sulphate and sodium hydroxide gave none of the required product.

1-*Methylglyoxaline*-5-*formaldehyde picrate* crystallises from water in yellow, elongated plates, m. p. 170° (corr.) (Found: C, 39·1; H, 2·7; N, 20·7. $C_5H_6ON_2,C_6H_3O_7N_3$ requires C, 38·9; H, 2·6; N, 20·7%). The corresponding base (IV) crystallised from alcohol in colourless prisms, but the quantity available was insufficient for its complete purification by reason of its hygroscopic character. It was very readily soluble in water, alcohol, ether, or chloroform.

The *nitrate* crystallises from water in colourless prisms, m. p. 175° (corr.; eff.). Its aqueous solution reacts acid to litmus [Found in salt dried at 100° (loss 2·2%): C, 34·4; H, 4·2. $C_5H_6ON_2,HNO_3$ requires C, 34·6; H, 4·1%].

Reduction. 1-Methylglyoxaline-5-aldehyde (0·34 g.), red phosphorus (0·004 g.), and hydriodic acid (2 c.c.) were heated for 6 hours at 160°. The product was mixed with water and extracted with chloroform, then the aqueous solution was saturated with potassium carbonate and again extracted with chloroform. This left an oil which was converted into picrate, and after recrystallisation from water 1 : 5-dimethylglyoxaline picrate (0·38 g.; yield, 38%; m. p. 168—169°) was obtained. It did not depress the m. p. of a known specimen of 1 : 5-dimethylglyoxaline picrate, but its mixtures with

1 : 4-dimethylglyoxaline picrate (m. p. 167—168°) and 1-methylglyoxaline-5-formaldehyde picrate (m. p. 170°) were depressed to 136—142° and 145—150°, respectively.

Oxidation. To 1-methylglyoxaline-5-aldehyde (0·48 g.) in water (5 c.c.), potassium permanganate (0·44 g.) and sulphuric acid (0·4 c.c.) in water (20 c.c.) were added. After 4 hours, the mixture was heated for ½ hour at 100°, then basified with sodium carbonate, filtered from inorganic matter, and extracted with chloroform. This took up unchanged aldehyde, which was recovered as picrate in 16% yield. The aqueous mother-liquor was rendered faintly acid and evaporated to dryness, and the residue was extracted with absolute alcohol. The extracted substance was mixed with alcoholic picric acid; *5-carboxy-1-methylglyoxaline picrate* then separated in 14% yield (0·24 g.; m. p. 197—198°). This salt crystallises from water in large, anhydrous, irregular leaflets, m. p. 198—199° (corr.; eff.). It is sparingly soluble in cold water or alcohol, but readily soluble in hot water (Found: C, 37·5; H, 2·5; N, 19·6.

$$C_5H_6O_2N_2,C_6H_3O_7N_3$$

requires C, 37·2; H, 2·5; N, 19·7%).

Action of potassium hydroxide. 1-Methylglyoxaline-5-formaldehyde (0·24 g.) was dissolved by warming with 50% aqueous potassium hydroxide (3 c.c.). The solution was kept for 24 hours, acidified faintly with hydrochloric acid, and evaporated to dryness. The residue was extracted with absolute alcohol, and picric acid added; *1-methyl-5-hydroxymethylglyoxaline picrate* (0·28 g.; m. p. 166°; yield, 37·5%) then separated first, followed by 5-carboxy-1-methylglyoxaline picrate (0·23 g.; m. p. 192—196°; yield, 30%). The latter did not depress the m. p. of an authentic specimen.

1-Methyl-5-hydroxymethylglyoxaline picrate crystallised from water in yellow prisms, m. p. 166° (corr.). It is sparingly soluble in cold water [Found in salt dried at 100° (loss 0·6%): C, 38·9; H, 3·3. $C_5H_8ON_2,C_6H_3O_7N_3$ requires C, 38·7; H, 3·2%].

4(5)-*Methylglyoxaline*-5(4)-*formaldehyde* (XII).—5(4)-Methyl-4(5)-hydroxymethylglyoxaline (8 g.) was oxidised by heating on the water-bath with nitric acid (12 c.c.; *d* 1·42), and the product was worked up as in the oxidation of the lower homologue (Pyman, J., 1916, **109**, 188); 4(5)-methylglyoxaline-5(4)-formaldehyde (4·5 g., crude; m. p. 150—160°; yield, 57%) and 4(5)-methylglyoxaline-5(4)-carboxylic acid (1·3 g., crude; m. p. 202°; yield, 14·4%) were then obtained. After recrystallisation from water, the acid formed clusters of long needles, m. p. 222—223° with effervescence. Gerngross (*loc. cit.*) gives m. p. 223°.

4(5)-*Methylglyoxaline*-5(4)-*formaldehyde* crystallises from water in anhydrous, colourless, elongated prisms, m. p. 167° (corr.). It is

sparingly soluble in cold water, but readily soluble in alcohol (Found: C, 54·8; H, 5·6. $C_5H_6ON_2$ requires C, 54·6; H, 5·5%). The *picrate* crystallises from water in anhydrous, yellow needles, m. p. 180—181° (corr.) (Found: C, 38·6; H, 2·8; N, 21·1. $C_5H_6ON_2,C_6H_3O_7N_3$ requires C, 38·9; H, 2·7; N, 20·7%). The anil, prepared from this aldehyde in the usual way, crystallised from alcohol in colourless plates, m. p. 224° (corr.) (Found: C, 71·2; H, 6·1. Calc.: C, 71·4; H, 5·9%). Gerngross (*loc. cit.*), who prepared this anil from 4(5)-methylglyoxaline-5(4)-glyoxylic acid, gives m. p. 224°.

Preparation of 1 : 4-*Dimethylglyoxaline*-5-*formaldehyde* (XIV).—(A) *By methylation of* 4(5)-*methylglyoxaline*-5(4)-*formaldehyde*. 4(5)-Methylglyoxaline-5(4)-formaldehyde (9·4 g.) and methyl sulphate (9·4 c.c.) were heated at 100° for 20 minutes. The product was mixed with aqueous sodium carbonate, and extracted with chloroform, which collected 5·24 g. of colourless needles, m. p. (crude) 50—70°. This was added to picric acid (12 g.) in methyl alcohol; 11·0 g. of pure 1 : 4-dimethylglyoxaline-5-formaldehyde picrate (yield, 36%) were then obtained. The aqueous alkaline liquor was neutralised with hydrochloric acid and evaporated to dryness, and the residue extracted with alcohol, which removed crude unmethylated aldehyde. This was purified as picrate, 5·1 g. (17% unchanged) being obtained.

(B) *By oxidation of* 1 : 4-*dimethyl*-5-*hydroxymethylglyoxaline*. 1 : 4-Dimethyl-5-hydroxymethylglyoxaline (2·77 g.) was oxidised with concentrated nitric acid (3 c.c.), and the product worked up for the aldehyde in the usual way; 2·5 g. (yield, 92%), m. p. 60—70°, were obtained.

1 : 4-*Dimethylglyoxaline*-5-*formaldehyde* crystallises from water in colourless, elongated prisms, containing $1H_2O$, which melt at 70° (corr.) after drying in a vacuum (Found: loss, 13·4. $C_6H_8ON_2,H_2O$ requires H_2O, 12·7%. Found in dried substance: C, 57·9; H, 6·3; N, 22·6. $C_6H_8ON_2$ requires C, 58·1; H, 6·5; N, 22·6%). It is very readily soluble in water, alcohol, or chloroform, and slightly soluble in ether. The *picrate* crystallises from water in small, yellow, anhydrous needles, m. p. 212—213° (corr.). It is almost insoluble in cold water, alcohol, or acetone (Found: C, 40·9; H, 3·2; N, 19·8. $C_6H_8ON_2,C_6H_3O_7N_3$ requires C, 40·8; H, 3·1; N, 19·8%).

Oxidation. 1 : 4-Dimethylglyoxaline-5-formaldehyde is very resistant to oxidation. It was recovered to the extent of 85% unchanged after heating with 10 parts of concentrated nitric acid for 5 hours at 120°, but could be oxidised to the carboxylic acid by means of acid permanganate. The aldehyde (0·8 g.) in water

(25 c.c.) was cooled with ice, and a solution of potassium permanganate (0·6 g.) and sulphuric acid (0·4 c.c. conc.) in water (50 c.c.) was added in the course of 2 hours. The solution was filtered, concentrated to small bulk, mixed with sodium carbonate, filtered from manganese carbonate, made faintly acid to methyl-orange with hydrochloric acid, and extracted with ether and chloroform, which removed unchanged aldehyde (0·33 g.; yield, 41%). The aqueous solution was evaporated to dryness under diminished pressure, and the residue extracted with absolute alcohol. The extract gave on evaporation a colourless solid (0·54 g.), which was converted into the picrate, and this crystallised from water, 1·08 g. of pure 5-carboxy-1 : 4-dimethylglyoxaline picrate being obtained; *yield*, 45%.

1 : 4-*Dimethylglyoxaline*-5-*carboxylic acid* crystallises from water in colourless, anhydrous needles, m. p. 205—206° (corr.; eff.) (Found: C, 51·3; H, 5·7. $C_6H_8O_2N_2$ requires C, 51·4; H, 5·7%). It is readily soluble in water or alcohol, but insoluble in ether or acetone. The *picrate* crystallises from water in small, yellow needles containing $1H_2O$ and after drying at 100° has m. p. 186—187° (corr.) (Found in air-dried salt: loss at 100°, 4·6.

$$C_6H_8O_2N_2,C_6H_3O_7N_3,H_2O$$

requires H_2O, 4·6%. Found in dried salt: C, 39·3; H, 3·0. $C_6H_8O_2N_2,C_6H_3O_7N_3$ requires C, 39·0; H, 3·0%).

Decarboxylation. When the acid (0·14 g.) was heated above its m. p., it effervesced and an oil distilled. The distillate and residue were combined, and converted into picrate. After crystallisation from water, 0·11 g. of a picrate (yield, 34%), m. p. 166—167°, was obtained, and identified as 1 : 4-dimethylglyoxaline picrate (m. p. 167—168°), since it did not depress the m. p. of this salt in admixture with it. A mixture of this picrate with 1 : 5-dimethylglyoxaline picrate (m. p. 168—169°) melted at 133—135°, and a mixture with 5-carboxy-1 : 4-dimethylglyoxaline picrate melted at 146—148°.

Action of potassium hydroxide. 1 : 4-Dimethylglyoxaline-5-formaldehyde (0·65 g.) was dissolved in a solution of potassium hydroxide (5·0 g.) in water (10 c.c.), and the mixture kept for 24 hours. The product was acidified faintly with hydrochloric acid and evaporated to dryness, and the residue extracted with absolute alcohol. Picric acid was added to the extract, and the picrates were crystallised fractionally; 1 : 4-dimethyl-5-hydroxymethylglyoxaline picrate (0·8 g.; m. p. 166—167°, alone or mixed with a known specimen; yield, 45%) and 5-carboxy-1 : 4-dimethylglyoxaline picrate (0·21 g.; m. p. 203—204°, alone or mixed with a known specimen; yield, 14%) were then obtained.

Methylation of Methyl Glyoxaline-4(5)-carboxylate.—Methyl glyox-
line-4(5)-carboxylate (4·5 g.) and methyl sulphate (4·5 c.c.) were nixed and warmed gently. After the vigorous reaction had sub-ided, the mixture was heated for ½ hour at 100°, then basified vith sodium carbonate, and extracted with chloroform. The hloroform on evaporation left an oil (3·1 g.), which was converted nto picrate, and this crystallised from methyl alcohol; 5-*carbo-nethoxy-1-methylglyoxaline* picrate (4·38 g.; m. p. 169°; yield, 2·6%) and 4(5)-carbomethoxyglyoxaline picrate (0·47 g.; yield, ·7%) were then isolated. The aqueous mother-liquor was neutral-sed with hydrochloric acid, and evaporated to dryness under liminished pressure. The residue was extracted with absolute lcohol and the extracted material was converted into picrate and ecrystallised from water; 4(5)-carboxy-1 : 3-dimethylglyoxalinium icrate (1·72 g., m. p. 216—217°; yield, 13·1%) was then obtained. n a subsequent experiment in which 9 g. of ester were methylated, ather better yields were obtained, namely, 37% of 5-carbomethoxy-·methylglyoxaline picrate, 26% of the picrate of the unchanged ster, and 16% of the 4(5)-carboxy-1 : 3-dimethylglyoxalinium icrate; in addition a very small quantity of picrate (0·24 g.; m. p. 171—172° [corr.]; yield, 0·9%) was isolated which was doubtless *nethyl 1-methylglyoxaline-4-carboxylate*, judging from the results of nalysis and the fact that it depressed the m. p. of the other products f the reaction (Found: C, 39·2; H, 3·0. $C_6H_8O_2N_2,C_6H_3O_7N_3$ equires C, 39·0; H, 3·0%). This substance crystallised from water n yellow prisms, m. p. 171—172° (corr.), which were sparingly oluble in cold water or alcohol.

Methyl 1-methylglyoxaline-5-carboxylate crystallises from absolute nethyl alcohol in colourless, elongated prisms, m. p. 68—70° corr.) (Found: C, 51·3; H, 5·8; N, 20·2. $C_6H_8O_2N_2$ requires C, 51·4; H, 5·7; N, 20·0%). It is soluble in water, alcohol, or hloroform, but sparingly soluble in cold ether.

The *picrate* crystallises from water in small, yellow, anhydrous risms, m. p. 171° (corr.) (Found: C, 39·3; H, 3·2; N, 18·7; OMe, ·1; NMe, 7·6. $C_6H_8O_2N_2,C_6H_3O_7N_3$ requires C, 39·0; H, 3·0; N, 19·0; OMe, 8·8; NMe, 7·9%). It is sparingly soluble in cold vater, methyl or ethyl alcohol.

4(5)-*Carboxy-1 : 3-dimethylglyoxalinium picrate* crystallises from vater in fine, yellow, anhydrous needles, m. p. 220—221° (corr.) Found: C, 39·3; H, 3·2; N, 19·2; OMe, nil; NMe, 15·5. $C_{12}H_{11}O_9N_5$ requires C, 39·0; H, 3·0; N, 19·0; 2NMe, 15·5%). t is sparingly soluble in cold water or alcohol. This salt was also repared by methylating pure methyl 1-methylglyoxaline-5-carb-

oxylate (1 g.) by heating with methyl sulphate (1 c.c.), hydrolysing the product with sodium hydroxide, and isolating the final product as picrate as previously described; yield, 54%.

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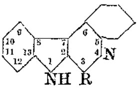
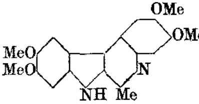
IV.—*Syntheses in the Indole Series. Part II. 5 : 6-Benz-4-carboline and its Derivatives.*

By WILLIAM OGILVY KERMACK and ROBERT HENRY SLATER.

IT has of recent years been shown that certain naturally occurring alkaloids are derivatives of 4-carboline. Methods for the synthesis of the analogous 5:6-*benz-4-carboline* (I; R = H) and its derivatives are now described. One derivative (II) of this base has been prepared by

(I.) 

 (II.)

Lawson, Perkin, and Robinson (J., 1924, **125**, 629) as a step in the synthesis of *apo*harmine, but their method is not generally applicable. The methods to be described render 5 : 6-benz-4-carboline and its homologues comparatively readily accessible and the detailed examination of the reactions and physiological properties of synthetic polynuclear bases of this type has thus become feasible.

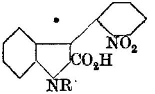
Two schemes were investigated for the synthesis of benzcarboline derivatives. In the first, an attempt was made by condensing *o*-nitrobenzyl chloride with ethyl acetoacetate, to obtain ethyl *o*-nitrobenzylacetoacetate, which it was thought might yield 3-methyl-5 : 6-benz-4-carboline (benzharman) (I; R = Me) by a similar method to that used by Manske, Perkin, and Robinson (J., 1927, 2) for the synthesis of harmaline. Under various conditions, however, the products of the condensation were the compound (m. p. 103°) formulated by Reissert (*Ber.*, 1896, **29**, 637) as $CH_3\cdot CO\cdot C(CO_2Et)(CH_2\cdot C_6H_4\cdot NO_2)_2$, and an *isomeride*, m. p. 183° which was insoluble in aqueous sodium carbonate but soluble in *sodium hydroxide solution. It is difficult to formulate the* latter otherwise than as

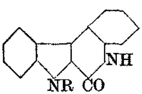
$$NO_2\cdot C_6H_4\cdot CH_2\cdot CH(C_6H_4\cdot NO_2)\cdot CH(CO_2Et)\cdot CO\cdot CH_3.$$

For the second scheme *o*-nitrophenylpyruvic acid was required in large quantities. The original method of preparation described by

:eissert (*Ber.*, 1897, **30**, 1036) gave yields of less than 50% and the rocedure necessary to obtain the pure crystalline acid was very ıborious and sometimes uncertain. We have found that, when ɔecial precautions are taken, Blaikie and Perkin's method (J., 924, **125**, 310), in which certain methoxy-derivatives of *o*-nitro-ɔluene are condensed with ethyl oxalate in ethereal solution in the resence of potassium ethoxide, can be utilised for the preparation f *o*-nitrophenylpyruvic acid in excellent yield and in a state of igh purity.

The phenylhydrazone of *o*-nitrophenylpyruvic acid (Reissert, *'er.*, 1897, **30**, 1038) readily underwent the Fischer indole condens-tion when its boiling alcoholic solution was saturated with dry ydrogen chloride. The resulting *ethyl* 3-o-*nitrophenylindole-·carboxylate* was converted through the *potassium* salt into the *acid* II; R = H), which was readily obtained in a pure condition. he alkaline mother-liquor from the preparation of the potassium ılt contained 3-o-*nitrophenylindole*, formed, apparently, during the ıdole cyclisation by loss of carbon dioxide: the amount formed aried with the duration of boiling during the saturation with

(III.) 

 (IV.)

ydrogen chloride; in some experiments a large yield was obtained ccompanied by very little acid. Attempts to increase the yield f the acid by carrying out the saturation at 50° did not lead to the esired result, since the potassium salt isolated after boiling with .coholic potassium hydroxide consisted mainly of that of the nchanged phenylhydrazone.

When 3-*o*-*nitrophenylindole-2-carboxylic acid or its calcium salt* as heated, some 3-*o*-nitrophenylindole was produced; the ammon-ım salt, however, decomposed smoothly at 270—280°, and 3-*o*-nitro-henylindole was obtained in very good yield.

3-*o*-Nitrophenylindole-2-carboxylic acid was reduced by zinc ust in acetic acid solution; ring closure also occurred, the product ɜing 3-*keto-3 : 4-dihydro-5 : 6-benz-4-carboline* (IV; R = H). The .cility with which ring closure takes place, even in an alkaline ɔlution, is shown by the fact that, in an experiment in which the ɜduction was carried out by means of ferrous sulphate and ammon-ım hydroxide so that the solution remained alkaline, no product : the reduction could be detected in the filtrate from the ferric oxide, ıt the product was obtained as the carboline derivative after ssolution of the ferric oxide in dilute hydrochloric acid.

The conversion of 3-keto-3 : 4-dihydro-5 : 6-benz-4-carboline (IV R = H) into 5 : 6-benz-4-carboline (I; R = H) presented difficultie and only when it was reduced with zinc dust in a current of hydroge could a small amount of the base be obtained. This and othe carboline bases, however, can be obtained, as described below, fron 3-*o*-nitrophenylindole.

The reduction of 3-*o*-nitrophenylindole to the correspondin amino-compound proceeds satisfactorily only under special con ditions. When it was reduced in acetic acid solution with zin dust, a non-basic substance, m. p. about 265°, was obtained, th constitution of which has not yet been elucidated. Owing, appar ently, to the insolubility of the nitrophenylindole in water, reductio with tin and hydrochloric acid or with stannous chloride solutio did not take place. When a solution of the compound in boilin alcohol containing hydrochloric acid was treated with tin, reductio occurred, but very little or none of the aminophenylindole could b isolated from the reaction product. It appeared that this difficult was due to the fact that the base forms very sparingly solubl compounds both with stannic salts and with hydrochloric acid an that the former are not readily decomposed by alkali. Ultimatel it was found that 3-o-*aminophenylindole* could be readily obtaine in good yield by reduction of the nitro-compound in alcoholi solution with iron and hydrochloric acid (compare West, J., 1925 **127**, 494).

When 3-*o*-aminophenylindole was refluxed with anhydrous formi acid 3-o-*formamidophenylindole* was obtained mixed with a smal quantity of 5 : 6-benz-4-carboline (I; R = H). The crude formy derivative itself, on treatment in boiling toluene with phosphory chloride, was converted into this base.

Various homologues of 5 : 6-benz-4-carboline were prepared in a similar manner, *e.g.*, 3-*methyl*-5 : 6-*benz*-4-*carboline* (I; R = Me from 3-o-*acetamidophenylindole*, which was obtained in excellen yield from 3-*o*-aminophenylindole in boiling acetic anhydride When 3-*o*-acetamidophenylindole was boiled for a long tim with acetic anhydride, with or without the addition of zinc chloride the extent of ring closure, as manifested by the appearance of a fluorescence, was so small that none of the benzcarboline could b isolated. Saturation of a solution of the acetyl derivative in alcoho with hydrogen chloride, and addition of phosphorus pentoxide to a solution in boiling benzene, were even less effective, as in neithe case was there even a development of the fluorescence.

3-Methyl-5 : 6-benz-4-carboline has many points of resemblanc to harman: it gives none of the usual indole reactions, but exhibit a marked blue fluorescence in acid solutions. It appears to be a

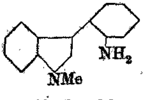
much weaker base than harman and it shows no tendency to absorb carbon dioxide from the atmosphere (compare diveratroharmyrine [II], which is so strongly basic that special precautions had to be taken to exclude carbon dioxide during its preparation). When precipitated from cold solutions it exhibits no tendency to form a gelatinous mass like that characteristic of the tetramethoxy-compound; this property of the latter compound, therefore, does not depend merely on the nuclear structure.

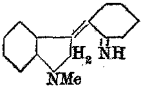
3-*o*-Propionamidophenylindole was converted by the phosphoryl chloride method into *3-ethyl-5 : 6-benz-4-carboline* (I; R = Et). Apart from a tendency to combine with and retain solvents, this compound closely resembles 5 : 6-benz-4-carboline and the methyl derivative in its properties.

Unlike *o*-nitrophenylpyruvic acid phenylhydrazone, *o-nitrophenylpyruvic acid phenylmethylhydrazone*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot C(CO_2H)\!:\!N\cdot NPhMe,$$

underwent the Fischer indole condensation when acted upon with dilute hydrochloric acid. This result is in accord with the general experience that hydrazones prepared from phenylmethylhydrazine undergo indole cyclisation with much greater ease that the corresponding ones obtained from phenylhydrazine. The product of the reaction was *3-o-nitrophenyl-1-methylindole-2-carboxylic acid* (III; R = Me), which is very similar in its properties to 3-*o*-nitrophenylindole-2-carboxylic acid; *e.g.*, it was converted by zinc dust and acetic acid into *3-keto-1-methyl-3 : 4-dihydro-5 : 6-benz-4-carboline* (IV; R = Me), and when heated to 250° it decomposed with evolution of carbon dioxide and formation of *3-o-nitrophenyl-1-methylindole*. This was reduced in alcoholic solution to the corresponding amino-compound by means of iron filings and hydrochloric acid. *3-o-Aminophenyl-1-methylindole* is peculiar in that it has an old-gold colour and is only sparingly soluble in alcohol and ether, whereas 3-*o*-aminophenylindole itself is colourless and is readily soluble in these solvents. Further, the *N*-methyl derivative melts 47° higher than the parent base; in all other cases the melting point of the methyl derivative is lower than that of the compound from which it is derived. These facts suggest that this compound may have a quinonoid structure and that its formula may be (VI) rather than (V).

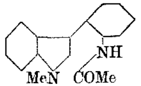
(V.) 

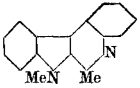
 (VI.)

3-o-Acetamidophenyl-1-methylindole (VII) was obtained in excellent

yield by acetylation of 3-*o*-aminophenyl-1-methylindole, and was readily converted into 1 : 3-*dimethyl*-5 : 6-*benz*-4-*carboline* (VIII) by boiling in toluene solution with phosphoryl chloride. This carboline derivative closely resembles 3-methyl-5 : 6-benz-4-carboline, and fluoresces strongly in acid solutions.

(VII.)





(VIII.)

These compounds are being studied from the point of view of the theory of anhydronium base formation in carboline derivatives, and it is hoped to submit the results in a future communication.

A consideration of the formula of 3-*o*-nitrophenylindole-2-carboxylic acid (III; R = H) suggests the possibility that the free rotation of the *o*-nitrophenyl group might be inhibited by the carboxyl group on the one hand and the projecting apex of the benzenoid ring on the other. It appears probable that the optical activity of certain diphenyl derivatives is occasioned by the absence of free rotation due to steric hindrance (compare Christie and Kenner, J., 1922, **121**, 614, *et seq.*), and it was therefore desirable to ascertain whether 3-*o*-nitrophenylindole-2-carboxylic acid could be resolved. The *brucine* salt was prepared, and this well-defined compound was recrystallised from alcohol but no sign of resolution was observed. The acid, when liberated carefully in the cold from its brucine salt, proved to be inactive. It seems, therefore, that the projecting apex of the benzenoid ring adjacent to the point of attachment of the *o*-nitrophenyl group is, in this case at least, insufficient to prevent free rotation.

EXPERIMENTAL.

Condensation of o-*Nitrobenzyl Chloride and Ethyl Acetoacetate.*—Ethyl acetoacetate (13 g.) was added to absolute ethyl alcohol (200 c.c.) in which sodium (2·3 g.) had been dissolved. To this mixture, cooled to 0°, was added *o*-nitrobenzyl chloride (8·6 g.) dissolved in the minimum quantity of alcohol, and the whole was allowed gradually to attain room temperature; sodium chloride then slowly separated. After 12 hours, the mixture was slightly acidified with 5% hydrochloric acid and steam-distilled, the residue was extracted with ether, and the combined ethereal extracts were shaken with 1% sodium hydroxide solution. The ethereal solution gradually deposited crystals of the compound, m. p. 103°, described by Reissert (*loc. cit.*). From the combined alkaline extracts, carbon dioxide precipitated a *substance* which, after several recrys-

tallisations from alcohol, was obtained in brownish-yellow, microscopic needles, m. p. 183° (decomp.) (Found: C, 60·0; H, 4·8; N, 6·6; *M*, ebullioscopic in alcohol, 371. $C_{20}H_{20}O_7N_2$ requires C, 60·0; H, 5·0; N, 7·0%; *M*, 400). It is very sparingly soluble in most of the usual organic solvents except boiling ethyl alcohol, in which it dissolves to the extent of about 2 parts in 100; the solution has an intense reddish-brown colour.

o-*Nitrophenylpyruvic Acid.*—In the preparation of this acid by the method described by Blaikie and Perkin (*loc. cit.*) it was found particularly important to cool the solution of potassium ethoxide (prepared from potassium, 19·6 g., and absolute alcohol, 24 g.) and ethyl oxalate (73 g.) in ether (500 c.c.) very efficiently before adding o-nitrotoluene (68·5 g.) in order to obtain satisfactory results. The total yield obtained from carefully dried reactants was 96 g. The acid crystallised from benzene in large, pale yellow, octagonal plates, m. p. 121° (compare Reissert, *Ber.*, 1897, **30**, 1037; Blaikie and Perkin, *loc. cit.*, p. 332), but a much purer product, m. p. 130°, decomposing at 140°, was obtained from alcohol.

o-Nitrophenylpyruvic acid phenylhydrazone was prepared by heating a mixture of the acid (8·4 g.) and phenylhydrazine (4·8 g.) in 50% acetic acid (70 c.c.) for 30 minutes on the steam-bath; the viscid oil that separated, after solidifying, crystallised from benzene in pale yellow, well-shaped prismatic needles (yield 10·2 g.), m. p. 153·5° (decomp.) (Reissert, *Ber.*, 1897, **30**, 1038, gives m. p. 148—149°).

The phenylhydrazone is readily soluble in alcohol or glacial acetic acid, moderately easily soluble in ether or boiling benzene, and almost insoluble in cold benzene or light petroleum. It is only slightly soluble in cold dilute sodium hydroxide or sodium carbonate solution, but dissolves slowly on warming, giving in the latter case a yellow solution from which the original material is deposited on cooling, and in the former case ultimately a blood-red solution which smells of phenylhydrazine and probably contains sodium *o*-nitrophenylpyruvate. The phenylhydrazone is insoluble in concentrated hydrochloric acid even on warming and no indication of the formation, by this treatment, of any indole derivative could be obtained.

3-o-*Nitrophenylindole-2-carboxylic Acid* (III; R = H).—A boiling alcoholic solution of the preceding phenylhydrazone was saturated with dry hydrogen chloride, ammonium chloride separating, and after hydrolysis of the oil which was precipitated on dilution with water 3-*o*-nitrophenylindole-2-carboxylic acid was isolated in the form of the sparingly soluble potassium salt.

The following method is more convenient in practice: A mixture of *o*-

nitrophenylpyruvic acid (80 g.), absolute ethyl alcohol (500 c.c.), and phenylhydrazine (50 g.) was boiled for 30 minutes and then cooled somewhat, and dry hydrogen chloride passed in; ammonium chloride and sometimes a brown solid separated, but the latter redissolved. The saturated mixture was boiled for 30 minutes, again saturated with dry hydrogen chloride, kept for a few hours, and then diluted with water (1000 c.c.). The oil that separated was isolated by means of ether and boiled for 30 minutes with a solution of potassium hydroxide (30 g.) in absolute alcohol (300 c.c.). After 12 hours, the reddish-orange crystals which had separated were collected, washed with absolute alcohol, and dried in the steam-oven (55 g.). The *acid*, liberated from this potassium salt, crystallised from benzene–absolute alcohol in pale yellow, rectangular, prismatic needles, m. p. 276° (decomp.) (Found: C, 64·1; H, 3·9; N, 9·8. $C_{15}H_{10}O_4N_2$ requires C, 63·8; H, 3·6; N, 9·9%).

3-*o*-*Nitrophenylindole-2-carboxylic acid* is insoluble in water, sparingly soluble in benzene or boiling chloroform, but is much more free soluble in alcohol. It dissolves readily in hot glacial acetic acid and crystallises, on cooling, in pale greenish-yellow rhombic plates. From a solution in cold dilute aqueous sodium or ammonium hydroxide, excess of the alkali precipitates the sodium or ammonium salt. The acid gives with *p*-dimethylaminobenzaldehyde and hydrochloric acid in alcoholic solution (Ehrlich's reagent) an orange coloration which is unchanged on prolonged boiling with excess of hydrochloric acid: no change is observed on addition of sodium nitrite to the cooled solution. The vanillin and the pine-shaving reaction are negative.

The *calcium* and the *barium* salt separate from water in sheaves of fine, long, golden-yellow needles and in large, yellow, well-shaped, rhombic plates respectively, and the bright yellow, crystalline *magnesium* salt in feathery rosettes. The amorphous, yellow *lead* and *zinc* salts are insoluble in hot water. The *brucine* salt separates readily when alcoholic solutions of the acid and of brucine are mixed and crystallises from alcohol in fine, bright yellow, rectangular, prismatic needles, m. p. 230° (Found: N, 8·4. $C_{15}H_{10}O_4N_2,C_{23}H_{26}O_4N_2$ requires N, 8·3%). $[\alpha]_D^{18°} = -50·5°$ in 1% chloroform solution.

When the alcoholic mother-liquor from which potassium 3-*o*-nitrophenylindole-2-carboxylate had separated was diluted with much water an orange-red substance (39 g.) was precipitated. (The filtrate gives no precipitate on the addition of hydrochloric acid, thus showing that the above method of separating 3-*o*-nitrophenylindole-2-carboxylic acid as its potassium salt is quantitative.) This was freed from a tarry impurity by solution in ether, and

recrystallised from light petroleum (b. p. 60—80°), containing a little benzene, 3-o-*nitrophenylindole* being thus obtained in long, bright orange, prismatic needles, m. p. 119° (Found: C, 71·0; H, 4·6; N, 11·5. $C_{14}H_{10}O_2N_2$ requires C, 70·6; H, 4·2; N, 11·8%).

3-*Keto*-3 : 4-*dihydro*-5 : 6-*benz*-4-*carboline* (IV; R = H).—Zinc dust (20 g.) was added gradually to a solution of 3-*o*-nitrophenylindole-2-carboxylic acid (6 g.) in boiling acetic acid (150 c.c. of 80%) and the whole refluxed during 30 minutes. The mixture was filtered while hot, and the residue extracted thrice with small quantities of boiling acetic acid. The combined filtrates were poured into an excess of water; the pale pink solid which separated (4·5 g.) crystallised from pyridine in snow-white, microscopic, rectangular, prismatic needles which showed no tendency to melt at 316° (Found: C, 76·4; H, 4·6. $C_{15}H_{10}ON_2$ requires C, 76·9; H, 4·3%).

The same substance was formed when a mixture of 3-*o*-nitrophenylindole-2-carboxylic acid (2·8 g.), ammonium hydroxide (14 c.c.; *d* 0·880), ferrous sulphate (18 g.), and water (40 c.c.) was boiled for 2 hours, and remained undissolved (1·2 g.) when the washed precipitate of iron oxide was dissolved in dilute hydrochloric acid.

3-*Keto*-3 : 4-*dihydro*-5 : 6-*benz*-4-*carboline* is practically insoluble in benzene, alcohol, and light petroleum even on boiling, but it is moderately easily soluble in hot glacial acetic acid and in pyridine. It is best recrystallised from the latter solvent, since its solution in acetic acid tends to develop a pink coloration when exposed to the atmosphere and the crystals deposited from such a solution are coloured. A fine blue fluorescence develops in an acetic acid solution and also when the compound is boiled with water containing a trace of hydrochloric acid.

This benzcarboline is in many respects similar to 3-keto-4-methyl-3 : 4-dihydro-4-carboline and other derivatives previously described (Kermack, Perkin, and Robinson, J., 1922, **121**, 1886; Blaikie and Perkin, *loc. cit.*, p. 319). With Ehrlich's reagent it gives no reaction in the cold, but a very faint green coloration develops on prolonged boiling with excess of concentrated hydrochloric acid; the colour fades on cooling and no further change is observed on addition of aqueous sodium nitrite. A faint green coloration, which does not change on prolonged boiling, is observed when this compound is treated with vanillin and hydrochloric acid. The pine-shaving test is negative.

3-o-*Nitrophenylindole*.—This compound, which was first obtained as described above, was also prepared by heating 3-*o*-nitrophenylindole-2-carboxylic acid in quantities of 2 g. at 275—280°, carbon dioxide being evolved; when the decomposition appeared to

be complete, the temperature was raised to 285—290°. Owing to resinification, the yield was very poor. Attempts to increase it by heating the acid with glycerol or quinoline, and by heating its calcium or potassium salt under atmospheric pressure or in a vacuum were unsuccessful. When, however, the ammonium salt was heated, in quantities of 2 g., at 270—280°, decomposition took place smoothly with evolution of carbon dioxide and ammonia. The product, after cooling, was dissolved in ether, and the ethereal solution shaken with small volumes of aqueous sodium carbonate (5%) to free it from unchanged acid. The subsequent purification of the nitrophenylindole was effected as described on p. 39 (yield 87%).

3-o-*Nitrophenylindole* has a slight indole odour, especially when heated, and is readily soluble in alcohol and benzene but much less soluble in light petroleum. With Ehrlich's reagent it develops after prolonged boiling with excess of concentrated hydrochloric acid, a faint pink colour, which fades on cooling. With vanillin and hydrochloric acid it gives a pink coloration on warming. The pine-shaving test is negative.

3-o-*Aminophenylindole*.—Iron filings (20 g.) were added in small portions during 30 minutes to a boiling solution of 3-o-nitrophenylindole (23·8 g.) in 90% alcohol (200 c.c.) containing concentrated hydrochloric acid (10 c.c.; *d* 1·19). Boiling was continued for 3 hours, sodium ethoxide (4 g. of sodium in 100 c.c. of alcohol) then added, and the liquid refluxed for a few minutes. The mixture of iron and ferric oxide was filtered off and extracted thrice with small quantities of boiling alcohol. The combined filtrate and extracts were submitted to steam-distillation to remove the alcohol; the aminophenylindole then separated as a brown oil which solidified on cooling. The crude base (17 g.) was freed from any unchanged nitro-compound by saturation of its ethereal solution with dry hydrogen chloride; the hydrochloride thus quantitatively precipitated was washed with a little alcohol, and the base was set free by the action of warm aqueous sodium hydroxide and isolated by means of ether as a yellow oil which solidified. Great difficulty was experienced in its further purification. It dissolved on warming in most organic solvents, but separated on cooling as an uncrystallisable oil. It decomposed below the b. p. when attempts were made to distil it under diminished pressure, pungent indole vapours being evolved. Ultimately, crystallisation was effected by dissolving the base in light petroleum (b. p. 80—100°) containing a little benzene, a few chips of potassium hydroxide being added to prevent formation of the carbonate of the base. The base separated partly as a yellow oil which slowly solidified and partly in fine, lo

colourless, rectangular needles, m. p. 82°; on further recrystallisation the melting point fell to 75°. The analytical results indicate that the compound was still not quite pure (Found: C, 79·5; H, 6·1. $C_{14}H_{12}N_2$ requires C, 80·8; H, 5·8%).

3-o-*Aminophenylindole* has a slight aniline odour. It is readily soluble in alcohol and benzene, but much less soluble in light petroleum. The *hydrochloride* forms pear-shaped plates, m. p. 288° (Found: Cl, 14·5. $C_{14}H_{12}N_2,HCl$ requires Cl, 14·5%), and is sparingly soluble in water; the solution has a very faint blue fluorescence. The *picrate*, prepared from the base and picric acid in benzene, crystallises from benzene in long, orange needles, m. p. 190°, decomp. 200° (Found: N, 15·8. $C_{14}H_{12}N_2,C_6H_3O_7N_3$ requires N, 16·0%). When 3-*o*-aminophenylindole is heated with chloroform and alcoholic potassium hydroxide no carbylamine odour is produced; acidification of the mixture does not give rise to a fluorescent solution. Ehrlich's reagent gives with this indole compound, on prolonged boiling in presence of concentrated hydrochloric acid, a faint pink coloration, which disappears on cooling. The addition of sodium nitrite to the cooled solution effects no change. Vanillin and hydrochloric acid give with this base a faint pink coloration in the cold, which changes to green on warming and fades on dilution. The pine-shaving test is negative. 3-*o*-Aminophenylindole hydrochloride is diazotised only very slowly and the diazotised solution gives a yellow precipitate with an alkaline solution of β-naphthol.

5 : 6-*Benz-4-carboline* (I; R = H).—3-*o*-Aminophenylindole (2·3 g.) was formylated by boiling under reflux with an excess of formic acid (98—99%) for 15 minutes. When the reaction mixture was poured into excess of water, the latter exhibited a brilliant bluish-green fluorescence due to the formation of a trace of 5 : 6-benz-4-carboline by the dehydrating action of the formic acid; this trace was precipitated on addition of excess of aqueous ammonia. The crude formyl derivative separated as an oil which solidified slowly (2 g.). It was boiled under reflux with perfectly dry toluene (8 c.c.) and freshly distilled phosphoryl chloride (5 c.c.) for 2 hours, hydrogen chloride being slowly evolved; as the reaction neared completion, a dark, viscid oil separated, which solidified on cooling. The liquor was decanted, the solid washed several times with light petroleum (b. p. 60—80°) and dissolved in an excess of alcoholic potassium hydroxide (20%), and the filtered solution poured into an excess of water; the resulting emulsion slowly deposited yellow, needle-shaped crystals of the benzcarboline (1·4 g.). This was dissolved in boiling dilute hydrochloric acid, reprecipitated by ammonia, and crystallised from benzene containing a little solid potassium hydroxide, 5 : 6-*benz-4-carboline*

being obtained in pale yellow, microscopic needles, m. p. 245° (Found: C, 82·9; H, 4·8. $C_{15}H_{10}N_2$ requires C, 82·6; H, 4·6%). The base gives none of the usual indole reactions, and in acid solutions it exhibits a beautiful bluish-green fluorescence.

5 : 6-Benz-4-carboline was also obtained when 3-keto-3 : 4-dihydro-5 : 6-benz-4-carboline (2·5 g.) was distilled over a large excess of zinc dust in a current of hydrogen. The small quantity of light brown oil that condensed in the unheated portions of the tube and slowly solidified crystallised from benzene in fine, needle-shaped crystals; it then melted at 243°, and at 244° in admixture with 5 : 6-benz-4-carboline prepared as described above.

3-Methyl-5 : 6-benz-4-carboline (I; R = Me).—A solution of 3-*o*-aminophenylindole (16 g.) in freshly distilled acetic anhydride (40 c.c.) was boiled under reflux for 30 minutes and then poured into much water; this acquired a fine blue fluorescence and 0·6 g. of the carboline was isolated from it. The aqueous mixture was warmed on the water-bath; the oil which separated solidified slowly after cooling (18·5 g.) and was then crystallised from aqueous alcohol, *3-o-acetamidophenylindole* being obtained in colourless, rhombic plates, m. p. about 158°. It is readily soluble in alcohol and benzene, but only sparingly soluble in light petroleum.

3-Methyl-5 : 6-benz-4-carboline was produced by the phosphoryl chloride method (see p. 41) (3-*o*-acetamidophenylindole, 7 g.; dry toluene, 30 c.c.; phosphoryl chloride, 15 c.c.). It was isolated (6 g.) in the same way as the lower homologue and crystallised from benzene–light petroleum (b. p. 60—80°) containing potassium hydroxide, separating in stellate clusters of pale yellow, prismatic needles, m. p. 204—205° (Found: C, 83·1; H, 5·5; N, 12·0. $C_{16}H_{12}N_2$ requires C, 82·8; H, 5·2; N, 12·1%).

3-Methyl-5 : 6-benz-4-carboline is readily soluble in alcohol, benzene, and chloroform, but much less soluble in light petroleum; the solutions exhibit a brilliant blue fluorescence. The *hydrochloride* crystallises in bright yellow needles and is sparingly soluble in water; the saturated solution exhibits a vivid green fluorescence, which becomes blue on dilution, and is considerably reduced in intensity on addition of sodium chloride. Picric acid and chloroplatinic acid precipitate from the hydrochloride solution the *picrate* in bright yellow, hexagonal plates and the *chloroplatinate* in flat, sharp-pointed, yellow plates.

3-Ethyl-5 : 6-benz-4-carboline (I; R = Et).—3-*o*-Aminophenylindole (20 g.) was boiled under reflux with an excess of propionic anhydride (or propionyl chloride and an excess of pyridine) for 30 minutes, and the crude dried propionyl derivative, obtained in the usual way, was refluxed in dry toluene (80 c.c.) for 2 hours with

phosphoryl chloride (40 c.c.). The product was worked up in the same way as the two lower homologues and recrystallised from benzene or ethyl acetate, 3-*ethyl*-5 : 6-*benz*-4-*carboline* (14·5 g.) being obtained in large, pale yellow, rectangular plates radially arranged, m. p. 158° with frothing. This frothing appears to be due to the loss of a small quantity of solvent of crystallisation and was observed even after prolonged heating of the crystals at 100° (Found : C, 82·0; H, 6·1. $10C_{17}H_{14}N_2,CH_3{\cdot}CO_2Et$ requires C, 82·0; H, 5·8%). 3-Ethyl-5 : 6-benz-4-carboline has an intense bluish-green fluorescence in acid solutions. It does not give the ordinary indole reactions.

3-o-*Nitrophenyl*-1-*methylindole*-2-*carboxylic Acid* (III; R = Me).—A solution of *o*-nitrophenylpyruvic acid (42 g.) in warm glacial acetic acid (150 c.c.) was diluted with an equal volume of boiling water, warmed for a few minutes with phenylmethylhydrazine (25 g.), treated with hydrochloric acid (200 c.c.; *d* 1·19), and heated on a boiling water-bath for 30 minutes. The yellow oil thus produced solidified (43 g.), and crystallised from a small volume of hot alcohol in bright yellow, rectangular, prismatic needles, m. p. 234° (decomp.) (Found : C, 65·1; H, 3·9. $C_{16}H_{12}O_4N_2$ requires C, 64·9; H, 4·1%).

3-o-*Nitrophenyl*-1-*methylindole*-2-*carboxylic acid* is insoluble in water, sparingly soluble in benzene, and moderately easily soluble in alcohol. When it is boiled with aqueous sodium or ammonium hydroxide, a small quantity dissolves and the remainder is converted into a reddish-orange compound—apparently the sodium or ammonium salt. The *calcium* salt crystallises from water in fine, bright yellow needles, and the *barium* salt in long, yellow, prismatic needles. The amorphous *lead* and *zinc* salts are insoluble in boiling water. The *magnesium* salt separates from a hot concentrated solution in orange, well-shaped, hexagonal plates. With Ehrlich's reagent the acid develops, on prolonged boiling with excess of concentrated hydrochloric acid, a faint pink coloration which disappears on cooling and no further change is observed on addition of sodium nitrite. With vanillin and hydrochloric acid a deep green coloration develops on warming, which persists on cooling but changes to yellow on dilution. The pine-shaving test is negative.

3-*Keto*-1-*methyl*-3 : 4-*dihydro*-5 : 6-*benz*-4-*carboline* (IV; R = Me).—Small quantities of zinc dust were added to a boiling solution of 3-*o*-nitrophenyl-1-methylindole-2-carboxylic acid (2·5 g.) in acetic acid (100 c.c.) until the colour was almost discharged. The mixture was refluxed for 10 minutes and filtered, the residual zinc dust repeatedly extracted with acetic acid until a test portion of the filtered extract, on dilution with water, showed hardly any opalescence, and the combined filtrate and washings, which showed a marked fluores-

cence, were diluted with water (4 vols.); the pink precipitate thus produced crystallised from pyridine in fine, white, felted needles, m. p. 302° (*Found*: N, 11·2. $C_{16}H_{12}ON_2$ requires N, 11·3%).

3-*Keto*-1-*methyl*-3 : 4-*dihydro*-5 : 6-*benz*-4-*carboline* is almost insoluble in water, alcohol, or benzene, but is slightly soluble in boiling glacial acetic acid, from which it separates in small needles on cooling. It is more soluble in hot pyridine; the solution exhibits a very slight blue fluorescence. Fluorescence is more marked in acetic acid and is also observed when a trace of the compound is boiled with water containing a little hydrochloric acid. The carboline gives none of the usual indole colour reactions.

3-o-*Nitrophenyl*-1-*methylindole*.—3-*o*-Nitrophenyl-1-methylindole-2-carboxylic acid decomposed at 250° with loss of carbon dioxide. The product was freed from unchanged acid by repeated extractions with boiling 5% sodium carbonate solution, dried (yield, 80%), and recrystallised from light petroleum (b. p. 80—100°) or alcohol, 3-*o*-*nitrophenyl*-1-*methylindole* separating in large, orange octahedra, m. p. 98° (Found: C, 71·4; H, 4·8; N, 11·2. $C_{15}H_{12}O_2N_2$ requires C, 71·4; H, 4·8; N, 11·1%).

This compound is readily soluble in benzene, chloroform, and glacial acetic acid, moderately easily soluble in alcohol, but only sparingly soluble in light petroleum. It gives a faint pink coloration with Ehrlich's reagent in the cold; the colour is intensified slightly on prolonged boiling with hydrochloric acid, but fades on cooling; the cooled solution gives an orange coloration with sodium nitrite. When the compound is treated with vanillin and hydrochloric acid a pink colour develops in the cold; on warming, this changes to a purple colour which persists on cooling but disappears on dilution. The pine-shaving test is negative.

3-o-*Aminophenyl*-1-*methylindole* (V and VI).—Iron filings (20 g.) were added in small quantities to a boiling solution of 3-*o*-nitrophenyl-1-methylindole (17 g.) in alcohol (400 c.c.) containing hydrochloric acid (10 c.c.). Boiling was continued for 3 hours and the reduction product was worked up as described in the case of 3-*o*-aminophenylindole, except that the hydrochloride was precipitated from benzene instead of ether, in which the base is rather sparingly soluble. The dried base (14·5 g.) crystallised from hot alcohol, containing a little aqueous ammonia, in large, old-gold, rectangular, prismatic needles, m. p. 129° (Found: C, 81·5; H, 6·3. $C_{15}H_{14}N_2$ requires C, 81·1; H, 6·3%).

3-o-*Aminophenyl*-1-*methylindole* is only slightly soluble in alcohol, light petroleum, and ether, but is readily soluble in benzene. The *hydrochloride* forms long, sharp-pointed, colourless plates, m. p. 248° (decomp.), slightly soluble in water, ether, and benzene but readily

soluble in alcohol. The *picrate* separates from alcohol in bright orange, hexagonal prisms, m. p. 196°, decomp. 205° (Found: N, 15·3. $C_{15}H_{14}N_2,C_6H_3O_7N_3$ requires N, 15·5%). The base gives with Ehrlich's reagent in the cold a faint pink coloration which is intensified slightly on boiling and fades on cooling; addition of sodium nitrite does not alter the colour. With vanillin and hydrochloric acid the base gives a pink coloration which is intensified on warming and fades on dilution. The pine-shaving test is negative. The hydrochloride of the base diazotises only very slowly and the diazotised solution gives an orange precipitate when treated with an alkaline solution of β-naphthol.

3-o-*Acetamidophenyl-1-methylindole* (VII).—3-*o*-Aminophenyl-1-methylindole (7·3 g.) was refluxed with an excess of acetic anhydride for 30 minutes, and the product isolated in the usual way; the water used acquired a fine green fluorescence due to the presence of a small quantity of carboline. The *acetyl* derivative (7 g.) crystallised from alcohol in long, pale yellow, hexagonal prisms, m. p. 159°. It is only sparingly soluble in alcohol, ether, and light petroleum, but readily soluble in benzene, chloroform, and glacial acetic acid. With Ehrlich's reagent a pale green colour develops on prolonged boiling with excess of concentrated hydrochloric acid; the colour fades on cooling and addition of sodium nitrite produces no further change. With vanillin and hydrochloric acid the acetyl derivative gives a faint purple coloration on warming, which persists on cooling. The pine-shaving test is negative.

1 : 3-*Dimethyl-5 : 6-benz-4-carboline* (VIII).—3-*o*-Acetamidophenyl-1-methylindole (4·5 g.), dissolved in dry toluene (40 c.c.), was refluxed for 2 hours with phosphoryl chloride (9 c.c.), and the *carboline* produced was worked up in the same way as the other homologues (yield, 2·9 g.). It crystallised from hot alcohol, containing a little aqueous ammonia, in long, pale yellow, rectangular plates, m. p. 154° (Found: C, 83·0; H, 5·7. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7%). It exhibits a beautiful green fluorescence in acid solutions, and gives none of the usual indole reactions.

The authors desire to express their thanks to the Department of Scientific and Industrial Research for a personal payment to one of them (R. H. S.) which has enabled this work to be carried out, and to the Government Grant Committee of the Royal Society for a grant which has defrayed part of the cost. For many of the analyses they are indebted to Mr. F. Hall, Oxford, and they also wish to thank Mr. W. Spragg for assistance in carrying out this work.

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V.—*An Investigation of the Oxidation of Certain Aliphatic and Aromatic Carbon Compounds by Means of the Dichromate Reaction.*

By HARRY ARK.

GREY (J., 1914, **105**, 2204) devised a method for estimating the total carbon in organic compounds which depended upon (*a*) the gasometric estimation of carbon dioxide, and (*b*) the determination of the acetic acid content in the residual liquid. This method was simplified by Guyot and Simon (*Compt. rend.*, 1920, **170**, 514) and by Grey (*Biochem. J.*, 1923, **17**, 768). Assuming Grey's observations, confirmed by Simon (*Compt. rend.*, 1925, **180**, 1405), the author has carried out a systematic investigation of the oxidation and has attempted to standardise the experimental conditions.

A solution of the substance in water (or acetic acid) is added to an excess of standard potassium dichromate solution, and concentrated sulphuric acid is added. Oxidation takes place almost immediately to carbon dioxide and water, and to acetic acid in addition when a CH_3·CH group is present with other carbon atoms. The reaction mixture is poured into water, and the excess of dichromate determined by *N*/2-ferrous sulphate. The reaction mixture selected was the following, being slightly modified as necessity demanded: 10 C.c. of 2*N*-potassium dichromate, 15 c.c. of water containing 0·1 g. of the compound, and 33 c.c. of concentrated sulphuric acid.

The "dichromate value" is the number of c.c. of *N*-potassium dichromate required for complete oxidation of 0·1 g. of substance. The results obtained are summarised below.

	Dichromate value.	
Alcohols.	Found.	Calc.
Methyl	18·74	18·74
Ethyl	8·69	8·69
Propyl	16·20	16·65
n-Butyl	21·20	21·62
*iso*Butyl	21·80	21·62
Amyl *	24·10	24·90
Ethylene glycol	16·04	16·10
Monobasic acids.		
Formic	4·35	4·34
Acetic	No oxidation.	
Propionic	8·37	8·10
n-Butyric	13·93	13·64
n-Valeric	17·30	17·50
*iso*Valeric	17·27	17·50
Diethylacetic	13·60	13·80

	Dichromate value.	
Dibasic acids.	Found.	Calc.
{ Tartaric	6·65	6·65
{ Racemic	6·05	6·65
Malic	9·02	8·95
Butylmalonic	15·92	15·00
{ Fumaric	10·40	10·34
{ Maleic	10·24	10·34
Cyclic compounds.		
Furfuryl alcohol	22·41	22·45
Amylene glycol	19·18	19·23
Aromatic compounds.		
Benzoic acid	23·08	24·60
Salicylic acid	19·86	20·28
Protocatechuic acid	15·72	16·88
*iso*Propoxybenzoic acid	20·40	20·73
Mandelic acid	21·82	22·87

* Using 20 c.c. of 2*N*-$K_2Cr_2O_7$ and 40 c.c. of conc. H_2SO_4.

Formic acid required only 16·0 c.c. of sulphuric acid, whilst with this concentration of acid, propionic acid was quite stable; it may thus be possible to estimate a mixture of formic, acetic, and propionic acids.

Exceptions.—Succinic acid is stable to the chromic acid unless the quantity of sulphuric acid exceeds 25 c.c., and succinamide, acetamide, urea, and α-amino*iso*butyric acid are unaffected.

Aldehydes gave inaccurate dichromate values.

Halogen compounds gave free halogens which vitiated the subsequent titration.

The imino-group is oxidised and the method is therefore inapplicable to compounds containing it.

Summary.

(1) Aliphatic and aromatic substances can in general be oxidised to carbon dioxide and water, or to acetic acid in addition if a $CH_3 \cdot CH$ group is present.

(2) This reaction can be used for the quantitative estimation of certain organic compounds, but others are either not oxidised or only partially so.

(3) Water or acetic acid must be used as solvent for the material to be analysed.

(4) Compounds containing hydroxyl groups are easily oxidised.

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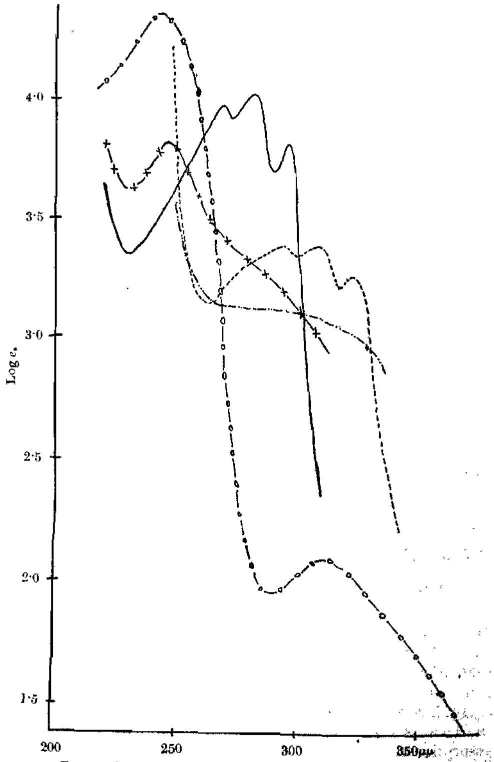
EGYPTIAN UNIVERSITY, CAIRO. [*Received, August 12th, 1927.*]

VI.—*Studies in the Sterol Group. Part I. The Absorption Spectra of Some Cholesterol Derivatives.*

By ISIDOR MORRIS HEILBRON, RICHARD ALAN MORTON, and WILFRED ARCHIBALD SEXTON.

THE pro-vitamin ergosterol, characterised by its well-defined absorption bands at 293·5 μμ, 281·5 μμ, and 270 μμ, is converted on irradiation into a photochemically unstable substance (vitamin D) giving an absorption band at 247 μμ (Morton, Heilbron, and Kamm, J., 1927, 2000). The work now to be described was undertaken with the view of correlating, if possible, unsaturation and ultra-violet absorption in the sterol group and obtaining some idea of the type of compound with which the vitamin may be classed. As previously mentioned (Morton, Heilbron, and Kamm, *loc. cit.*), it is very doubtful whether the formation of the vitamin is due to polymeris-

Fig. 1.



——— *Ergosterol.* —×—×— *Irradiated ergosterol.* - - - - - *α-Cholesterilene.*
—·—·— *Irradiated α-cholesterilene.* —o—o— *Cholestenone.*

ation of the ergosterol, and it is also unlikely, in view of the total alteration of the type of selective absorption, that the reaction is due simply to stereochemical changes in the molecule, for *cis-* and *trans-*isomerides usually differ in extinction rather than the general shape of the absorption curve (Henri and Errera, *Compt. rend.*, 1925, **180**, 2049; **181**, 548).

The following cholesterol derivatives have been examined spectrographically :

Compound.	Double bonds.	Types of absorption.
Cholesteryl chloride	1	No marked selective absorption.
Cholesteryl acetate	,,	,, ,, ,,
Cholesterol (pure)	,,	,, ,, ,,
Cholestene	,,	,, ,, ,,
ψ-Cholestene	,,	,, ,, ,,
Dicholesteryl ether	2	,, ,, ,,
Cholestenone	,, (one being C:O)	Bands at 243 μμ and 312 μμ.
Cholesterilene	2	Bands well-defined at 294 μμ, 304 μμ, and 321 μμ.
Oxycholesterylene	3 (one being C:O)	Band at 277 μμ.
Ergosterol	3	Bands at 270 μμ, 281·5 μμ, and 293·5 μμ.

Selective absorption is only shown when at least two double bonds are present in the single molecule. In comparison with Mauthner's cholesterilene the maximum absorption for each of the three bands of ergosterol is some 250 Å. units further in the ultra-violet :

Maxima for cholesterilene	*3210*	*3040*	*2940*
,, ,, ergosterol	2935	2817	2690
Differences	275	223	250

The molecular extinction coefficients are of the order : ergosterol, 10,000; cholesterilene, 2400. The shifting of the absorption bands in the direction of the ultra-violet region and the greatly increased extinction coefficient of the former compound, due to the introduction of an additional double bond, are quite in harmony with general views on absorption spectra. It seems reasonable to infer from these results that of the three double bonds in ergosterol two occupy the same positions as in cholesterilene.

The case of cholestenone is of interest. Whereas the shallow band at 312 μμ is probably an ordinary ketone band, that at 243 μμ is strikingly similar to the well-defined band 247 μμ of vitamin *D*. The irradiation of cholestenone in alcoholic solution resembles that of the vitamin in that the absorption band at 243 μμ disappears rapidly; the ketone band disappears less rapidly. On irradiation, no new bands are shown either by cholestenone or by any of the cholesterol derivatives showing selective absorption, although in all cases photochemical decomposition occurs. It is a well-established

fact that cholesterol readily undergoes intramolecular rearrangement, the type of compound isolated depending upon the conditions. The fundamental reaction, however, would appear to be dehydrogenation, leading to cholestenone formation (unpublished work), and it may well be that the passage of ergosterol into the vitamin follows a somewhat similar course, giving rise to ergostantrienone or a partly hydrogenated ketone derived from this. Although no band has been observed in the case of the vitamin in the region corresponding to the 312 $\mu\mu$ band of cholestenone, this does not preclude its possible occurrence, for owing to the incomplete transformation of ergosterol into vitamin a band in this region would be masked. Its presence may, however, be inferred from the fact that the photolabile vitamin continues to decompose even when screened by vita glass (Heilbron, Kamm, and Morton, *Nature*, October 29th, 1927).

Rosenheim and Webster (*Lancet*, September 17th, 1927) have stated that ergosteryl acetate and benzoate can be rendered antirachitic on irradiation, but this in no way refutes our arguments, for photochemical hydrolysis could readily precede photo-oxidation. That ergosterol is, indeed, extraordinarily sensitive to oxidative processes has recently been shown by Windaus, Borgeaud, and Brunken (*Nachr. Gess. Wiss. Göttingen*, 1927), who have fonnd that ergosterol is both readily dehydrogenated to a pinacol and photo-oxidised to a peroxide by sunlight in presence of suitable catalysts.

EXPERIMENTAL.

Cholesterol was obtained from cod-liver oil and repeatedly crystallised from alcohol; it had m. p. 148·5°, and $[\alpha]_D^{20°}$ −39·08° in chloroform ($c = 2·124$).

The derivatives were all prepared by the standard methods described in the literature. Cholesteryl chloride, m. p. 96°, was made by the action of thionyl chloride on cholesterol (Diels and Blümberg, *Ber.*, 1911, **44**, 2848). Cholesterilene and dicholesteryl ether were prepared by heating cholesterol with anhydrous copper sulphate (Mauthner and Suida, *Monatsh.*, 1896, **17**, 29). The cholesterilene was repeatedly crystallised from ether–alcohol until the m. p. (78°) remained constant; it had $[\alpha]_D^{20°}$ − 102·1° in chloroform ($c = 4·000$). Mauthner and Suida give m. p. 79—80° and $[\alpha]_D$ − 81·63°. The dicholesteryl ether, after twice crystallising from ethyl acetate containing a little benzene, melted at 194—195°.

Cholestenone was prepared by oxidation of cholesterol dibromide and subsequent debromination (Windaus, *Ber.*, 1906, **39**, 518). Recrystallisation from methyl alcohol gave a product melting sharply at 79° (Windaus gives 81—82°), which was characterised by the preparation of its semicarbazone, m. p. 234°. Oxycholesterylene

was prepared by oxidation of cholesteryl acetate (Mauthner and Suida, *Monatsh.*, 1896, **17**, 579). After repeated crystallisation from 80% alcohol, it had a constant m. p. of 110° (Mauthner and Suida give 112°).

Cholestene was prepared by the action of sodium and amyl alcohol upon cholesteryl chloride (von Fürth and Felsenreich, *Biochem. Z.*, 1915, **69**, 416). After repeated crystallisation from ether–alcohol it melted at 90—91°; the specific rotation, $[\alpha]_D$ − 53·05° (c = 3·544), was not affected by further crystallisation (von Fürth and Felsenreich give − 55·5°). It was further characterised by means of its isomeric α- and β-dibromides, m. p. 140° and 106°, respectively (Mauthner, *Monatsh.*, 1894, **15**, 85). ψ-Cholestene was prepared from cholestene hydrochloride (Mauthner and Suida, *Monatsh.*, 1907, **28**, 1113). After repeated crystallisation from ether–alcohol it melted at 78—79° and gave the dibromide, m. p. 116°, as described. It had $[\alpha]_D$ + 60·13° in chloroform (c = 3·176). Mauthner and Suida give + 64·86° for the same concentration, whereas Dr. A. Triebs of Münich finds + 57·3° (private communication). It is clear that the whole question of optical rotations in the cholesterol group of compounds is an extraordinarily complex one, and the specific rotations give no sure criteria of purity; *e.g.*, values of $[\alpha]_D$ ranging − 61·55° to − 116·2° have been found for cholesterilene, prepared in different ways (Windaus, *Z. physiol. Chem.*, 1921, **117**, 156). It is obvious that these anomalous results must arise from the complex nature of the cholesterol molecule, which contains numerous asymmetric carbon atoms, in any one of which racemisation may occur.

In conclusion we beg to thank the Council of the Department of Scientific and Industrial Research for a grant to one of us (W. A. S.) which has enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, September 16th, 1927.*]

VII.—*Nor-*d*-ψ-ephedrine, an Alkaloid from* Ephedra *Species.*

By SYDNEY SMITH.

FURTHER examination of the alkaloids from Ma Huang, a drug obtained from an *Ephedra* species collected in Northern China, has led to the isolation of a new subsidiary alkaloid in addition to l-methylephedrine recently described (Smith, J., 1927, 2056). The alkaloid is crystalline, forms well-defined crystalline salts and has the properties of a primary base. It has the empirical formula

$C_9H_{13}ON$ and since it forms *d*-ψ-methylephedrine *methiodide* on treatment with methyl iodide it must be *nor*-d-ψ-*ephedrine*, $OH{\cdot}CHPh{\cdot}CHMe{\cdot}NH_2$.

Nor-*d*-ψ-ephedrine forms a *monobenzoyl* and a *dibenzoyl* derivative. The monobenzoyl derivative is non-basic, but when it is warmed with dilute hydrochloric acid and alcohol, or kept for some time in acetone solution with hydrogen chloride, a transference of the benzoyl group from nitrogen to oxygen occurs with the formation of O-*benzoylnor*-d-ψ-*ephedrine hydrochloride*. This salt is stable and may be crystallised from water without decomposition. When it is treated with alkali, the original *N*-benzoyl derivative is recovered.

A similar migration of the acyl group in this type of compound has been recorded in the case of the *p*-nitrobenzoylephedrines (Seizo Kanao, *J. Pharm. Soc. Japan*, 1927, 20).

EXPERIMENTAL.

The syrupy alkaloidal residue obtained in the manufacture of ephedrine, freed as completely as possible from *l*-ephedrine, was diluted with water and fractionally precipitated with aqueous potassium hydroxide. After removal of successive crops of crystalline material consisting mainly of *d*-ψ-ephedrine, the fractions became oily. The final mother-liquor was extracted with ether, and the ethereal solution dried over potassium carbonate. The residue after removal of the ether was distilled under diminished pressure. The product was neutralised with 20% sulphuric acid and concentrated under diminished pressure; the sulphate of the new base then separated. *Nor*-d-ψ-*ephedrine sulphate* after repeated crystallisation from water separates in elongated, hexagonal plates. The m. p. varies with the rate of heating, but when placed in a bath at 290° and slowly heated the salt melts at 295° (corr.; decomp.) [Found: S, 8·1. $(C_9H_{13}ON)_2,H_2SO_4$ requires S, 8·0%]. It has $[\alpha]^{20^\circ}_{5461}$ + 42·9° in water (c = 1·0).

Nor-d-ψ-*ephedrine*, prepared by addition of potassium hydroxide to a solution of the sulphate and extraction with ether, crystallises readily from benzene in plates, m. p. 77—78° (corr.). It has $[\alpha]^{20^\circ}_{5461}$ + 32·2° in methyl alcohol (c = 2·89). The base is fairly easily soluble in water and in most organic solvents. It can be titrated with standard sulphuric acid and methyl-red (0·5606 g. required 37·0 c.c. of 0·1N-sulphuric acid. Calc., 37·1 c.c. Found: C, 71·6; H, 8·7. $C_9H_{13}ON$ requires C, 71·5; H, 8·7%).

When heated with excess of methyl iodide and potassium carbonate in dilute methyl alcohol, it gave a mixture of bases and a crystalline methiodide, m. p. 216—217° (corr.). There was no depression of the m. p. when the methiodide was mixed with

d-ψ-methylephedrine methiodide. The specific rotation in water was that of *d*-ψ-methylephedrine methiodide, $[\alpha]_{5461}^{20^\circ}$ + 36·8° (c = 2·4) (Found : I, 39·7. Calc. for $C_{12}H_{20}ONI$: I, 39·5%).

Nor-d-ψ-*ephedrine hydrochloride* was prepared by passing hydrogen chloride into a solution of the base in methyl alcohol. On addition of ether the salt separated in plates, m. p. 178—179° (corr.) (Found : Cl, 18·7. $C_9H_{13}ON,HCl$ requires Cl, 18·9%).

Nor-d-ψ-*ephedrine hydrogen tartrate*, prepared in aqueous solution, crystallises in needles. After drying in a vacuum at 95°, it melts at 149—151° (corr.) and has $[\alpha]_{5461}^{20^\circ}$ + 43·0° (in water; c = 1·7). The air-dried salt loses on complete drying 5·7% (Calc. for

$$C_9H_{13}ON,C_4H_6O_6,H_2O:$$

H_2O, 5·6%. Found for the dry salt: C, 51·9; H, 6·4. $C_9H_{13}ON,C_4H_6O_6$ requires C, 51·8; H, 6·4%).

Dibenzoylnor-d-ψ-*ephedrine*, prepared from benzoyl chloride, the base, and excess of potassium hydroxide solution, crystallised from dilute acetone or benzene in plates, m. p. 156—157° (corr.). $[\alpha]_{5461}^{20^\circ}$ + 28·0° (c = 2·2 in methyl alcohol) (Found: C, 76·5; H, 5·9. $C_{23}H_{21}O_3N$ requires C, 76·8; H, 5·9%).

N-*Benzoylnor*-d-ψ-*ephedrine* may be prepared by the partial hydrolysis of the dibenzoyl derivative. The latter (3 g.) was boiled for 1 hour with *N*-methyl-alcoholic potassium hydroxide (100 c.c.). The solution after concentration was diluted with water and extracted with ether, and the ethereal extract washed first with water and then with 5% hydrochloric acid. The ethereal solution after drying over potassium carbonate gave on evaporation a crystalline residue, m. p. 131—132° (yield, 1·8 g. Theoretical, 2·1 g.). It separated from solution in ethyl acetate with a little light petroleum in silky hairs, m. p. 132° (corr.). $[\alpha]_{5461}^{20^\circ}$ + 58·3° (c = 2·9 in methyl alcohol) (Found : C, 75·3; H, 6·7. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7%). When it is kept for some hours in contact with hydrogen chloride in acetone, crystals of a *hydrochloride* separate. The same salt may be obtained by warming the monobenzoyl derivative with dilute hydrochloric acid and alcohol until solution is effected; on cooling, the hydrochloride separates in needles, m. p. 244—245° (corr.; decomp.). $[\alpha]_{5461}^{20^\circ}$ − 32·5° (c = 0·9 in water) (Found: Cl, 12·4. $C_{16}H_{17}O_2N,HCl$ requires Cl, 12·2%). If a solution of the hydrochloride in water is precipitated with sodium hydroxide, the *N*-benzoyl derivative, identified by the m. p. and specific rotation, separates.

The author's thanks are due to Mr. W. Ramsay for assistance in this investigation.

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VIII.—*The Condensation of* cyclo*Hexanealdehyde and Malonic Acid.*

By Sarbbani Sahay Guha Sircar.

The well-known condensation between aldehydes and compound of the malonic acid type can proceed in three different directions depending on the conditions employed, giving rise to products of th types (I), (II), and (III), but in very few cases have all thre

(I.) $R{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$ $\qquad$ $R{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$ (III.)

(II.) $R{\cdot}CH_2{\cdot}CH{<}{}^{CH_2{\cdot}CO_2H}_{CH_2{\cdot}CO_2H}$ $\qquad$ $R{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO$ (IV.) (with CH and CO joined through O)

possibilities been realised. Products of type (I) are the mos common and are obtained in the presence of pyridine and piperidine Substances of the second type have been obtained from acetaldehyd and propaldehyde by Kommenos (*Annalen*, 1883, **218**, 145), usin acetic anhydride as the condensing agent. Instances of the con densation of one molecule of an aldehyde with two molecules o malonic, acetoacetic or acetonedicarboxylic ester and allied com pounds are, however, widely distributed in the literature (Claisen Crismer, Kommenos, Knoevenagel).

Ott (*Ber.*, 1891, **24**, 2600), by heating propaldehyde and maloni acid in acetic acid, obtained a mixture of two unsaturated acids The structures he assigned to them were corrected by Viefhau (*Ber.*, 1893, **26**, 915) on the evidence of oxidation experiments The presence of the unsaturated $\beta\gamma$-acid in the mixture obtained b Kommenos was detected by Fittig (*Ber.*, 1893, **26**, 2079), who als established the interconversion of the $\alpha\beta$- and $\beta\gamma$-acids in th presence of boiling alkali and suggested that the β-hydroxy-acid act as the intermediate in the transformation. Weinstein (*Annalen* 1885, **227**, 31) made a similar assumption. The isolation of th respective β-hydroxy-acids from the products obtained by treatin phenyl*iso*crotonic acid (Luib), phenyl-Δ^{β}-pentenoic acid (Hoffmann) Δ^{β}-*iso*heptenoic acid (Fittig and Feuer), and hydrosorbic aci (Fittig and Baker) with boiling alkali supports the view that th β-hydroxy-acid is the first product of the condensation of propalde hyde and malonic acid, and that the two unsaturated acids ar derived from it by dehydration proceeding in two differen directions. The $\beta\gamma$-acid, however, is the sole product of the con densation of phenylacetaldehyde and malonic acid (Linstead an Williams, J., 1926, 1735).

The condensation of *cyclo*hexanealdehyde has now been found t give a substance of the type (I), (II), or (IV) as the main produc according to the conditions of the experiment. In the presence o

pyridine and piperidine (or diethylamine), β-cyclo*hexylacrylic acid* (type I) was almost exclusively obtained. When a mixture of the aldehyde and malonic acid was heated on the steam-bath with a few drops of diethylamine, β-cyclo*hexylglutaric acid* (type II) was formed in good yield together with a small quantity of the unsaturated αβ-acid. In the presence of alcohol and a larger quantity of diethylamine (1 mol.), the product consisted mainly of cyclo*hexane*-spiro*butyrolactone* (type IV) mixed with a little of the αβ-acid. The presence of this acid in all the mixtures is no doubt due to its great stability, which is also displayed in its behaviour towards acids and alkalis. For example, although the lactone on long boiling with alkali passed into the αβ-acid, the conversion of the latter into the βγ-form or into its own geometrical isomeride has not been detected. The structures of the two unsaturated acids have been established by preparing them from the corresponding ketones described by Kon (J., 1926, 1798).

EXPERIMENTAL.

β-cyclo*Hexylacrylic acid* was prepared by the method described by Haworth, Perkin, and Rankin (J., 1924, **125**, 1693), *cyclo*hexanealdehyde being used in place of piperonal. It separated as an oil when the reaction product was poured into dilute hydrochloric acid, and, after solidifying, crystallised from dilute alcohol in scales, m. p. 57—58°, b. p. 153—154°/11 mm. (yield, 12 g. from 10 g. of aldehyde). It is very soluble in the usual organic solvents, including petroleum (b. p. 40—60°), very sparingly soluble in water, and can be purified by steam distillation (Found : C, 70·0; H, 9·1. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%. Found in the *silver* salt : Ag, 41·1. $C_9H_{13}O_2Ag$ requires Ag, 41·4%). The *acid chloride* boils at 142°/12 mm., the *methyl* ester at 92—93°/15 mm. (Found : C, 71·3; H, 9·8. $C_{10}H_{16}O_2$ requires C, 71·5; H, 9·5%) and the *ethyl* ester at 119°/11 mm. The *amide* melts at 158—159° (Found : C, 70·5; H, 9·9. $C_9H_{15}ON$ requires C, 70·6; H, 9·8%), and the *anilide* at 142°.

When the acid (1 mol.) was boiled for 24 hours with 64% caustic potash solution (20 mols.) or concentrated hydrochloric acid, little or no change occurred. Treatment with three parts of 50% sulphuric acid for 15 minutes gave rise to tarry products, but no lactone indicating conversion into the βγ-form could be isolated from the steam distillate.

The *dibromide*, formed in glacial acetic acid, was a thick colourless liquid which could not be distilled (9 mm.) without losing hydrogen bromide (Found : Br, 50·5. $C_9H_{14}O_2Br_2$ requires Br, 50·95%).

The unsaturated acid is immediately oxidised by dilute permanganate solution, and in a current of steam *cyclo*hexanealdehyde is obtained in good yield (semicarbazone, m. p. 175°).

β-cyclo*Hexylglutaric Acid*.—A mixture of *cyclo*hexanealdehyde (10 g.), malonic acid (20 g.), and diethylamine (1 c.c.) was kept for 12 hours, the acid gradually dissolving and the mixture separating into two layers, the lower of which increased in volume at the expense of the upper. The mixture was then heated on the steam-bath until effervescence ceased (1 hour) and finally gently refluxed for 10 minutes. The cooled product was poured into dilute hydrochloric acid, and the somewhat pasty solid obtained, after being removed and dried in ether, was extracted twice with petroleum (b. p. 40—60°) at the ordinary temperature. The residue crystallised from benzene or dilute alcohol in needles, m. p. 153—154° (yield, 12 g.). From the petroleum solution 3 g. of *cyclo*hexylacrylic acid were isolated by extraction with aqueous sodium bicarbonate and acidification.

β-cyclo*Hexylglutaric acid* is sparingly soluble in benzene, less so in water, and almost insoluble in petroleum. It crystallises from hot hydrochloric acid in scales (Found: C, 61·35; H, 8·6. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·4%. Found in the *silver* salt: Ag, 49·65. $C_{11}H_{16}O_4Ag_2$ requires Ag, 50·0%). The *acid chloride* boils at 159—160°/12 mm., the *methyl* ester at 106—108°/17 mm. (Found: C, 64·1; H, 9·4. $C_{13}H_{22}O_4$ requires C, 64·5; H, 9·1%), and the *ethyl* ester at 118—120°/17 mm. The *diamide* melts at 190° (Found: C, 62·05; H, 9·2. $C_{11}H_{20}O_2N_2$ requires C, 62·3; H, 9·4%). The *dianilide* is very sparingly soluble in ordinary solvents and crystallises in needles, m. p. 237° (decomp.), from methyl alcohol–acetone. The *anhydride* is a liquid which solidifies in ice. The *anilic acid* crystallises from dilute alcohol in needles, m. p. 151° (Found: C, 70·8; H, 7·9. $C_{17}H_{23}O_3N$ requires C, 70·6; H, 8·0%). It does not lose water below 185°, but when kept at 200° for a few minutes it changes into the *anil* (probably polymolecular; compare Auwers, *Annalen*, 1896, **292**, 132), which crystallises from dilute acetone in needles, m. p. 181°.

Oxidation of Hexahydrobenzylideneacetone.—The two unsaturated ketones (αβ and βγ) obtained by the condensation of *cyclo*hexanealdehyde with acetone (Kon, *loc. cit.*) were each oxidised with alkaline hypobromite solution as described by Barbier and Léser (*Bull. Soc. chim.*, 1905, **33**, 815). From 10 g. of the αβ-ketone (b. p. 103°/9 mm.), after removal of bromoform and excess of hypobromite, and acidification, 3 g. of unchanged ketone and 5 g. of an oily acid were obtained. The latter, after crystallising from dilute alcohol, was identical with *cyclo*hexylacrylic acid, m. p. 57—58° (Found: C, 69·65; H, 8·8; *Ag in silver salt*, 41·15. Calc.: C, 70·1; H, 9·1; Ag, 41·4%). On treatment with dilute permanganate solution it at once generated *cyclo*hexanealdehyde.

From the βγ-ketone (5 g., b. p. 101°/9 mm.), 2 g. of a liquid acid and 1·5 g. of unchanged ketone were obtained. The *βγ-acid* was purified through the *silver* salt but failed to solidify in a freezing mixture (Found in a sample that had been kept in a vacuum desiccator for 2 days: C, 69·7; H, 8·7. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%. Found in the silver salt: Ag, 41·5. $C_9H_{13}O_2Ag$ requires Ag, 41·4%). The acid had an odour resembling that of the lactone described below, but could not be distilled owing to the small quantity available. When kept in contact with dilute permanganate solution for a few minutes, it generated *cyclo*hexanone.

cyclo*Hexane*spiro*butyrolactone*.—A mixture of *cyclo*hexanealdehyde (10 g.), malonic acid (10 g.), diethylamine (10 c.c.), and alcohol (12 c.c.), after being warmed until the white solid first formed redissolved, was kept over-night and then heated on the steam-bath until effervescence ceased (1 hour). The cooled product was poured into dilute hydrochloric acid and the precipitated oil was taken up in ether, washed with bicarbonate solution, dried over potassium carbonate, and distilled. The *lactone* was obtained as a colourless, *mobile oil, b. p. 152—155°/15 mm., together with a small quantity* of a lower-boiling fraction (120—125°/15 mm.) containing the ester of the αβ-acid (Found: C, 69·8; H, 9·25. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%. Found for the *silver* salt of the corresponding hydroxy-acid: Ag, 39·4. $C_9H_{15}O_3Ag$ requires Ag, 38·7%).

The lactone is very sparingly soluble in water and unusually stable towards ammonia and dilute alkali solutions; even after 4—5 hours' refluxing with concentrated aqueous ammonia, a portion was undissolved. In making the silver salt, this portion was removed in ether before silver nitrate was added. The salts of the hydroxy-acid tend to lose water and pass into the salts of the unsaturated acid; this accounts for the high value of silver in the estimation. When a 10% solution of sodium hydroxide was boiled for 24 hours with the lactone and then acidified, the unsaturated αβ-acid, m. p. 57—58°, was isolated in good yield.

The exact conditions for the formation of the lactone are difficult to define, as in one or two experiments this was not produced, the unsaturated acid being obtained instead.

The author wishes to thank Professor J. F. Thorpe, C.B.E., F.R.S., and Dr. G. A. R. Kon for their kind interest in the work, and the Research Fund Committee of the Chemical Society for a grant that has partly defrayed its cost.

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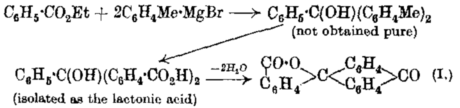
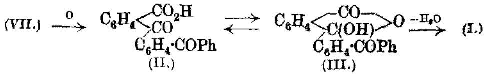
IX.—*A Cyclic Semipinacolin.*

By James Wilfred Cook.

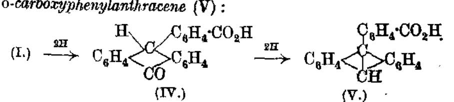
The action of moist silver oxide on benzylideneanthrone dibromid (VI) leads to a compound, $C_{21}H_{14}O_2$, which gives an acetyl derivativ and a coloured sodium salt, but is not 9-benzoylanthrone (Cook J., 1926, 2164). The structure of this compound has now bee more closely examined and it has been established that its formatio is due to a semipinacolin change * having converted the central rin of the anthracene complex into a seven-membered ring. Th experimental proof of this interpretation is based on the fact tha oxidation led to a monobasic acid which must be *2-benzoylbenzo phenone-2′-carboxylic acid* (II), since on dehydration it passed int a spirocyclic *lactone* (I), the structure of which was established b its synthesis from ethyl benzoate and magnesium *o*-tolyl bromid as follows :



The conversion of the acid (II) into the spirocyclic lactone i doubtless due to the acid being in equilibrium with the hydroxy phthalide (III), a phenomenon that is exhibited by ketonic acids o benzophenone-*o*-carboxylic acid type and accounts for their con version into acetyl derivatives (compare von Pechmann, *Ber.*, 1881, **14**, 1865; Graebe, *Ber.*, 1900, **33**, 2027), such an *acetat* (derived from III) being formed by the acid under discussion :



Further confirmation of the structure of the spirocyclic lactone was furnished by its reduction to 9-o-*carboxyphenylanthrone* (IV) and 9-o-*carboxyphenylanthracene* (V) :



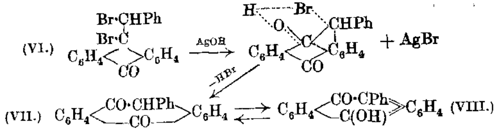
* This term has been used by Tiffeneau and Orékhoff (*Bull. Soc. chim.*, 1921, **29**, 424) to indicate the rearrangement of a *sec. tert.* glycol into a ketone by dehydration and migration. The product of such a change is conveniently termed a semipinacolin.

That a pinacolin type of rearrangement can be brought about by treatment of a *vic.*-dibromide with moist silver oxide has been shown by Couturier (*Ann. Chim. Phys.*, 1892, **26**, 448), who converted tetramethylethylene dibromide into pinacolin by this means, but it is remarkable that rupture of the anthracene complex should take place under the very mild conditions employed. That the anthracene complex is, in some circumstances, less stable than is generally supposed * is shown by the fact that anthraquinone monoxime undergoes the Beckmann rearrangement with the formation of a seven-membered ring, the oxime of the resulting compound yielding an eight-membered ring by a further Beckmann change (Beckmann and Liesche, *Ber.*, 1923, **56**, 16).

Evidence is found in the literature (*e.g.*, Couturier, *loc. cit.*; Zelinsky and Zelikow, *Ber.*, 1901, **34**, 3249; Thörner and Zincke, *Ber.*, 1878, **11**, 67; Zincke and Tropp, *Annalen*, 1908, **362**, 250; Werner and Grob, *Ber.*, 1904, **37**, 2899; compare Meerwein, *Annalen*, 1913, **396**, 249; 1914, **405**, 129) that the pinacolin change is reversible, the reduction of a β-pinacolin frequently resulting in the formation of a derivative of the pinacol. In the anthracene derivative described above, the change is undoubtedly of a reversible character, since the reduction of the semipinacolin (VII) with hydriodic acid yields 9-benzyl-9 : 10-dihydroanthracene.

The very mild conditions which suffice to convert the six-membered ring in benzylideneanthrone dibromide into the seven-membered ring render it improbable that the change is effected by dehydration of the glycol, and it appears more likely that the reaction consists in the first place in the replacement of one bromine atom by a hydroxyl group, subsequent removal of a molecule of hydrogen bromide from the resulting bromohydrin taking place concurrently with change in ring structure. On Robinson's theory of the mechanism of the pinacolin and Wagner–Meerwein transformations (*Mem. Manchester Phil. Soc.*, 1920, **64**, No. 4) the change can be represented by the following formulæ in which dotted lines represent partial valencies and imply that an electron belonging to one atom participates transiently in the electronic orbits of both atoms to which the first atom is attached by means of partial valencies:

* Robinson, in commenting on the formation of α-anthrapinacolin described by Barnett and Matthews (*J.*, 1923, **123**, 380), has suggested (*Ann. Reports*, 1923, **20**, 122) that the compound is really a β-pinacolin containing a seven-carbon ring. This speculation appears to be devoid of any experimental basis and is not in agreement with facts, as Matthews (private communication) has found that the oxidation of the pinacolin gives anthraquinone in far larger quantity than would be anticipated from Robinson's formula.



The resulting diketone (VII) forms a monoxime, and also yields a monoacetate and hence must be capable of *enolisation*. This may involve either of the carbonyl groups, but the intense red colour of the alkali-metal salts of the enol renders the orthoquinoid structure (VIII) the more probable.

Reduction of the diketone (VII) led to the formation of a *dihydro-compound*. This did not give an oxime but did give a diacetate and was soluble in sodium hydroxide solution to give a colourless sodium salt and hence is probably represented by the enolic formula $C_6H_4<\substack{C(OH):CPh \\ CH(OH)}>C_6H_4$ (IX).

Compounds of the phenyldeoxybenzoin type usually undergo hydrolytic fission very readily under the influence of alcoholic potassium hydroxide (compare Cook, J., 1926, 1679). Both the diketone (VII) and its dihydro-compound (IX) resisted attempts to effect ring fission by this means, although six-membered cyclic pinacolins have frequently been found to undergo this hydrolysis (*e.g.*, see Klinger and Lonnes, *Ber.*, 1896, **29**, 2155), and the stability of the seven-membered ring in the compounds now described is in harmony with modern views respecting the stability of *cyclo*heptane derivatives (Mohr, *J. pr. Chem.*, 1921, **103**, 316; Meerwein, *ibid.*, 1922, **104**, 177; Meerwein and Schäfer, *ibid.*, 1922, **104**, 289; Baker and Ingold, J., 1923, **123**, 122).

The enlargement of ring systems during pinacolin transformations has, of course, been observed, and numerous examples of the conversion of monocyclic five- and six-membered carbon rings into larger rings have been cited by Meerwein and his collaborators (Meerwein and Unkel, *Annalen*, 1910, **376**, 152; Meerwein, *ibid.*, 1913, **396**, 200; 1918, **417**, 255; Meerwein and Schäfer, *loc. cit.*).

A study of the absorption spectra of some of the compounds here described was initiated, but was not proceeded with, as the semi-pinacolin, its sodium salt and its acetyl derivative all showed only general absorption in the ultra-violet region of the spectrum. The red sodium salt also had an absorption band in the visible region.

The author desires to express his thanks to Messrs. E. B. Robertson, B.Sc., and C. P. Stein, B.Sc., for having photographed the absorption spectra of these compounds.

EXPERIMENTAL.

Rearrangement of Benzylideneanthrone Dibromide.—The con-itions already described (Cook, *loc. cit.*) for the preparation of the emipinacolin (VII) were found to give the best results, and the roduct was conveniently obtained free from anthraquinone by cidifying a filtered aqueous solution of the sodium salt. In one xperiment, in which 85 g. of benzylideneanthrone dibromide were reated with moist silver oxide, a 35% yield of the pure semi-inacolin was obtained and the residues, on oxidation, gave a 25% ield of 2-benzoylbenzophenone-2′-carboxylic acid (II) and a 30% ield of anthraquinone. The proportion of material converted nto the seven-membered ring compound was thus 60%. The use f acetone as a solvent is not essential, since the transformation also ccurred in the presence of alcohol.

A *monoxime* was obtained when the semipinacolin (VII; 2 g.) as heated in alcoholic solution (25 c.c.) for 2 hours with hydroxyl-mine hydrochloride (2 g.) and sodium acetate (3 g.) dissolved in a ttle water. The resulting solution was diluted somewhat, and he product twice recrystallised from aqueous alcohol. The resulting olourless needles, m. p. 191—193°, contained nitrogen (Found: ', 80·2; H, 4·9. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8%).

Reduction of the Semipinacolin (VII).—(a) The substance (5 g.) as intimately mixed with zinc dust (15 g.) and heated on the water-ath for 3 hours with concentrated ammonia (100 c.c.) diluted with ater (50 c.c.). The solid in suspension was collected, dried, and xtracted with ether. After removal of the ether, the residue was ecrystallised twice from benzene-light petroleum (yield, 3·3 g.), nd finally from toluene. The *dihydro-compound* (IX) formed a olourless, crystalline powder, m. p. 186—188° after sintering and ecoming yellow at 178°. It gave a colourless solution in boiling queous sodium hydroxide, but was unaffected by sodium carbonate Found: C, 83·9; H, 5·6. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3%).

This dihydro-compound (1 g.) yielded a *diacetate* when heated n the water-bath for an hour with acetic anhydride (2 c.c.) in yridine (3 c.c.). After two recrystallisations from alcohol the iacetate formed colourless plates, m. p. 154—156° (Found: C, 8·1; H, 5·3. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%).

The dihydro-compound (IX) was recovered unchanged after eating for 2 hours in alcoholic solution with hydroxylamine hydro-hloride and sodium acetate, and after boiling for ½ hour with 10% lcoholic sodium hydroxide solution. It yielded a resinous product hen reduced with sodium and boiling amyl alcohol. An acid was lso formed, but purification was difficult and the amount obtained

too small for investigation. Oxidation of the dihydro-compound with chromic acid in boiling acetic acid yielded 2-benzoylbenzophenone-2′-carboxylic acid.

(b) The semipinacolin (1 g.) was heated in a sealed tube at 190° for 7 hours with 50% hydriodic acid (15 c.c.) and red phosphorus (0·6 g.). The resulting solid was extracted with boiling alcohol. The alcoholic filtrate, on cooling, deposited 0·5 g. of pure 9-benzyl-9 : 10-dihydroanthracene, identified by direct comparison with an authentic sample (Cook, J., 1926, 1681).

Oxidation of the Semipinacolin (VII).—(a) On addition of potassium ferricyanide to a cold aqueous solution of the potassium salt of the semipinacolin the red colour was immediately discharged. The resulting gelatinous precipitate could not be obtained crystalline and was not further investigated.

(b) A boiling solution of the semipinacolin (20 g.) in acetic acid (200 c.c.) was treated slowly with an aqueous solution of chromic acid (50 g.). Boiling was continued for ½ hour, and the solution diluted with water; the precipitate was collected, extracted with sodium carbonate solution, and the filtrate acidified with hydrochloric acid. The precipitate was recrystallised from acetic acid, aqueous alcohol, and finally from xylene. *2-Benzoylbenzophenone-2′-carboxylic acid* (II) forms colourless needles, m. p. 228° (Found: C, 76·3; H, 4·5. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·2%). Fusion with potassium hydroxide yielded only benzoic acid.

The *methyl* ester was obtained when the acid (2 g.) was heated on the water-bath for 4 hours with methyl alcohol saturated witl hydrogen chloride (20 c.c.). It separated on cooling and afte recrystallisation from methyl alcohol formed colourless, glistenin needles, m. p. 165° (Found: C, 76·4; H, 4·7. $C_{22}H_{16}O_4$ require C, 76·7; H, 4·65%). This ester was recovered unchanged afte heating on the water-bath for an hour with acetic anhydride i pyridine and was reconverted by hydrolysis into the original acid These results are in accordance with the structure assigned to th acid, since a hydroxyl group, if present, would scarcely hav resisted both methylation and acetylation.

2-Benzoylbenzophenone-2′-carboxylic acid reacted with hydroxy amine in alkaline solution, but the product could not be purifie

An *acetate* (derived from III) was obtained when 2-benzoy benzophenone-2′-carboxylic acid (1 g.) was heated for an hour c the water-bath with acetic anhydride (1 c.c.) in pyridine (4 c.c. When the cooled solution was diluted with water an oil separat which slowly solidified. The product was washed with cold dilu sodium carbonate solution and with water and recrystallised fro alcohol. *o-Benzoylphenylacetoxyphthalide* forms small, colourle

needles, m. p. 171—173° (Found: C, 73·9; H, 4·5. $C_{23}H_{16}O_5$ requires C, 74·2; H, 4·3%).

Reduction of 2-Benzoylbenzophenone-2′-carboxylic Acid.—With the object of obtaining 1-benzylanthrone, or a derivative by subsequent ring closure, attempts were made to reduce this acid to 2-benzyldiphenylmethane-2′-carboxylic acid. This result appeared to be achieved by reduction with zinc dust and boiling sodium hydroxide solution, but the resulting acid could not be obtained crystalline and dehydration with sulphuric acid was accompanied by considerable oxidation and sulphonation.

Reduction with zinc dust and boiling acetic acid for 4 hours gave a yellow pasty substance which could not be purified, together with a small amount of an acid. This acid was extracted with sodium carbonate solution and then reprecipitated and crystallised twice from benzene. The product formed yellowish, microscopic needles, m. p. 213—214° (Found: C, 79·6; H, 5·2. $C_{21}H_{16}O_3$ requires C, 79·7; H, 5·1%).

Spirocyclic Lactone of 9-o-*Carboxyphenyl*-9-*hydroxyanthrone* (I).—A solution of 2-benzoylbenzophenone-2′-carboxylic acid (10 g.) in concentrated sulphuric acid (100 c.c.) was heated at 160° for ¾ hour. After cooling, the solution was poured into water, and the precipitate collected. The precipitate was recrystallised from acetic acid containing a little chromic acid, the purpose of the latter being to destroy a trace of coloured impurity. The product was quite pure (yield, 8 g.), but for analysis a sample was recrystallised from benzene–light petroleum (Found: C, 80·6; H, 3·9. $C_{21}H_{12}O_3$ requires C, 80·7; H, 3·85%). This *lactone* forms colourless needles, m. p. 238—239°; the m. p. was depressed by admixture with 1-benzoylanthraquinone.* The lactone was hydrolysed by boiling alcoholic potassium hydroxide, giving a solution which remained clear on dilution. From this solution the lactone was reprecipitated by the addition of a mineral acid.

9-o-*Carboxyphenylanthrone* (IV).—A boiling solution of the spirocyclic lactone (I; 2 g.) in acetic acid (25 c.c.) was treated with granulated tin (2 g.) and concentrated hydrochloric acid (4 c.c.), slowly added. After boiling for 1½ hours, the clear yellow solution was decanted from the excess of tin, diluted with a little water, and cooled. The resulting yellow solid was evidently the anthranol, but it passed into the anthrone and became colourless when warmed

* The crude lactone, but not the purified product, gave a green colour when its solution in sulphuric acid was treated with copper bronze. The green solution yielded a violet precipitate on dilution, and this colour reaction is taken as indicating the presence of a trace of 1-benzoylanthraquinone (formed by loss of water from II) in the crude dehydration product (compare Schaarschmidt, *Ber.*, 1915, 48, 837).

with benzene. Recrystallisation from benzene gave 9-o-*carboxyphenylanthrone* as colourless needles, m. p. 226—227° (Found C, 80·2; H, 4·6. $C_{21}H_{14}O_3$ requires C, 80·2; H, 4·5%). This anthrone gave an intense bluish-green colour when warmed with concentrated sulphuric acid, and dissolved in sodium carbonate solution with liberation of carbon dioxide to give the orange-yellow solution characteristic of an anthranol.

9-o-*Carboxyphenylanthracene* (V).—The spirocyclic lactone (I; 2 g.) was intimately mixed with zinc dust (6 g.) and heated on the water bath with concentrated ammonia (20 c.c.), diluted with water (10 c.c.), for 3 hours. After cooling, the solid was collected, the excess of zinc extracted with hydrochloric acid, and the residue recrystallised from acetic acid containing hydrochloric acid. The resulting colourless, glistening needles were recrystallised from benzene–light petroleum and finally from alcohol and then melted at 250—251° (Found: C, 84·3; H, 4·85. $C_{21}H_{14}O_2$ requires C, 84·6; H, 4·7%). This acid formed sparingly soluble salts with the alkali metals, and dilute solutions of these salts had a violet fluorescence.

Synthesis of the Spirocyclic Lactone (I) *of* 9-o-*Carboxyphenyl-9-hydroxyanthrone*.—(a) *Phenyldi*-o-*tolylcarbinol*. Ethyl benzoate (11·5 g.) was added to a Grignard solution prepared from o-bromotoluene (34 g.) and magnesium (4·8 g.), cooled in a freezing mixture. After addition of the ester, the ethereal solution was boiled for 3 hours and then decomposed with ice and hydrochloric acid. The ethereal layer was washed, the ether distilled off, and volatile by-products removed from the residue by steam distillation. The resulting viscous oil gave an orange-red solution in sulphuric acid; its solution in light petroleum yielded the corresponding chloride when treated with hydrogen chloride, and the chloride easily reacted with pyridine to give a quaternary salt. None of these products, however, could be obtained in a crystalline condition.

(b) *Lactonic acid of triphenylcarbinol*-2 : 2′-*dicarboxylic acid*. The crude phenyldi-o-tolylcarbinol (10 g.), prepared as described above, was suspended in a little potassium hydroxide solution and treated with a solution of potassium permanganate (25 g.) in water (500 c.c.). The whole was boiled for 16 hours, the small amount of residual permanganate removed by the addition of alcohol, and the precipitated hydroxides of manganese, which were contaminated with a considerable amount of unchanged carbinol, removed by filtration. The filtrate was acidified, and the resulting precipitate recrystallised successively from aqueous acetic acid, aqueous alcohol and aqueous acetic acid (Found: C, 76·4; H, 4·5. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·2%). This *lactonic acid* formed colourl

needles, m. p. 225—227°, and yielded a methyl ester which could not be purified on account of its excessive solubility and tendency to become resinous.

(c) *Dehydration of the lactonic acid.* A solution of the lactonic acid (0·5 g.) in concentrated sulphuric acid (5 c.c.) was heated at 160° for ½ hour. The cooled solution was poured into water and the precipitate was collected, extracted with dilute sodium hydroxide solution, and recrystallised from acetic acid. The resulting colourless needles melted at 238—239° and were shown to be identical with the spirocyclic lactone (I) prepared by dehydration of 2-benzoylbenzophenone-2′-carboxylic acid.

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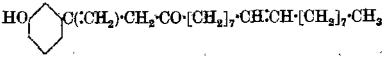
X.—*Campnospermonol, a Ketonic Phenol from* Campnospermum brevipetiolatum.

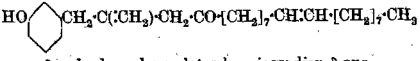
By THOMAS GILBERT HENRY JONES and FRANK BERRY SMITH.

Campnospermum brevipetiolatum (N.O. *Anacardiaceæ*), a large tree endemic in the Sepik River district, Mandated Territory of New Guinea, is stated by C. E. Lane Poole ("Forest Resources of the Territories of Papua and New Guinea," p. 106) to yield on tapping an oily exudate used by the natives as a substitute for coconut oil.

This material, received through the instrumentality of Mr. Lane Poole, consists principally of a ketonic phenol, $C_{27}H_{42}O_2$ or $C_{28}H_{44}O_2$, of phytochemical interest because of the association of the oleyl radical with an aromatic residue and possible generic connexion with the fatty oils, and represented by one of the constitutional formulæ



β-*m*-hydroxyphenyl-$\Delta^{\alpha\mu}$-heneicosadien-δ-one

and 

β-*m*-hydroxybenzyl-$\Delta^{\alpha\mu}$-heneicosadien-δ-one,

the results of investigation failing to distinguish between these. The ketonic phenol, which we propose to designate *campnospermonol*,

is conveniently isolated in the form of the more stable *methyl* ethe by distillation of the latter under reduced pressure.

It is characterised chemically by solubility in caustic alkal reactivity with acetic anhydride, and capacity for oxime formatior The iodine values and the ready addition of four atoms of hydroge under the influence of platinum as catalyst afford evidence of th existence in campnospermonol and campnospermonyl methyl ethe of two ethenoid linkages. That neither linkage is conjugated wit respect to the carbonyl group follows from the non-occurrence c the usual reactions of αβ-unsaturated ketones and from the norn ality of the molecular refraction.

Ready oxidation of campnospermonyl methyl ether in co acetone solution by means of potassium permanganate produc *m*-methoxybenzoic, azelaic, formic, and nonoic acids, the last-nam in quantitative yield. No dibasic acid other than azelaic w detected. Definite evidence of the attachment of a methyle group in the chain is the production of formic acid by oxidation wi ozone of the methyl ether in chloroform, there being obtained al nonoic acid and nonoaldehyde, together with long-chain acid ai aldehydic substances the constitutions of which were not expe mentally ascertained.

Reduction of campnospermonyl methyl ether by hydrogen presence of platinum produced *hydrocampnospermonyl methyl eth* $C_{28}H_{48}O_2$ or $C_{29}H_{50}O_2$, a crystalline ketone, yielding a crystalli *oxime* and producing on oxidation in acetone by potassium p manganate *m*-methoxybenzoic, margaric, and oxalic acids.

The acid product of the action of phosphorus pentachloride the oximino-derivative of hydrocampnospermonyl methyl etl consisted largely of stearic acid with a smaller amount of undet mined, presumably aromatic, acid. Accidental loss of the bulk the nitrile simultaneously produced in this reaction precluded ot than its cursory examination. The mixture of acids obtained hydrolysis of the nitrile was mainly aromatic, but contained a sn amount of fatty acid, probably margaric. The results, wl indicating that the oximino-derivative probably consisted of t isomerides, one in preponderating amount, serve, from the fac the direct production of stearic acid, to fix the position of carbonyl group definitely as indicated in the chain.

Conclusive evidence has not been obtained as to the exact c stitution of that portion of the chain comprising the attac methylene group and situated between the carbonyl group and aromatic nucleus, although the acetyl value (128) determined crystalline *hydrocampnospermonyl acetate* appears to favour the 1 of the formulæ proposed.

Reduction of the carbonyl group of campnospermonyl methyl ether to methylene by Clemmensen's method (*Ber.*, 1913, **46**, 1837) and subsequent hydrogenation of the ethenoid linkages yielded the saturated methoxy-hydrocarbon, β-*m*-methoxyphenylheneicosane or β-*m*-methoxybenzylheneicosane.

Further work on campnospermonol and its derivatives is contingent on the receipt of additional material. In view of the remoteness of the source of supply, however, postponement of publication of the results already obtained is deemed inadvisable.

EXPERIMENTAL.

The exudate, a dark, somewhat viscous liquid having the superficial characteristics of a fatty oil, an odour reminiscent of the higher fatty acids, and the constants $d^{15\cdot5^\circ}$ 0·9604, $n_D^{20^\circ}$ 1·489, acetyl value 125, and acid value 17, dissolved almost completely in dilute caustic alkali solution, whence 3% of resinous material was extracted by ether, and the phenolic constituent was liberated by passage of carbon dioxide.

Alternatively, the phenol was separated by extraction with ether after neutralisation of acid substances with an equivalent of alkali, or by acetylation and removal of acids by alkali extraction.

The ketonic phenol (*campnospermonol*) distilled at 260°/5 mm. with some decomposition as an amber, oily liquid that gave no distinctive coloration with ferric chloride; it had $d^{15\cdot5^\circ}$ 0·9454 and $n_D^{20^\circ}$ 1·4925 (Found: C, 81·2; H, 10·5. $C_{27}H_{42}O_2$ requires C, 81·4; H, 10·7%).

Campnospermonyl acetate had $d^{15\cdot5^\circ}$ 0·9550, $n_D^{20^\circ}$ 1·489, and b. p. 255—260°/5 mm.

Campnospermonol oxime distilled with some decomposition at 240°/5 mm.; $d^{15\cdot5^\circ}$ 0·9195; $n_D^{20^\circ}$ 1·489 (Found: N, 3·0%).

Campnospermonyl Methyl Ether.—Since the methyl ether was deemed best adapted for investigation, the bulk of the oil was methylated with methyl sulphate and sodium hydroxide, a small amount of acid material removed by hydrolysis of the ester and extraction of the alkali salt, and the residue distilled. The light yellow, oily *ether* distilled constantly at 240°/5 mm., appeared homogeneous, and had $d^{15\cdot5^\circ}$ 0·9342, $n_D^{20^\circ}$ 1·4960, iodine value 131, $[R_L]_D$ 128·8 (calc. for $C_{28}H_{44}O_2$, 128·8) (Found: C, 81·3; H, 10·7; OMe, 7·5.* $C_{28}H_{44}O_2$ requires C, 81·5; H, 10·7; OMe, 7·3%. $C_{29}H_{46}O_2$ requires C, 81·7; H, 10·8%).

The stable *oxime* had b. p. 215°/4 mm., $d^{15\cdot5^\circ}$ 0·9010, and $n_D^{20^\circ}$ 1·478 (Found: N, 3·2. $C_{29}H_{47}O_2N$ requires N, 3·2%).

* On analyses alone, formulæ comprising 26 to 29 carbon atoms could not be excluded for campnospermonol and its derivatives.

Oxidation Products of Campnospermonyl Methyl Ether.—(a) The methyl ether (200 g.) in acetone (500 c.c.) at 0° was oxidised with potassium permanganate (440 g.). After removal of the acetone, which left no residue on evaporation, the manganese dioxide was repeatedly treated with boiling water, the solution of potassium salts concentrated to small bulk and acidified with dilute sulphuric acid, a considerable amount of volatile acid distilled in steam, and the residual liquor thoroughly extracted with ether, finally in a continuous extractor. All the acids were converted into ethyl esters and fractionally distilled.

The bulk of the esters (90 c.c.) of acids volatile in steam distilled at 96—98°/10 mm. and had the constants of ethyl nonoate, $d^{15.5°}$ 0·8700, $n_D^{20°}$ 1·420, b. p. 222°/760 mm.; the recovered acid was identified as nonoic acid by the percentage of silver (40·8) in the silver salt, by formation of the characteristic barium nonoate, and by preparation of the amide (m. p. 99·5°). The nonoic ester recovered corresponded practically to one-third of the weight of the methyl ether [illegible]

Formic acid was detected by qualitative tests in the distilled acid liquor after extraction of nonoic acid with ether.

The esters of acids not appreciably volatile in steam were separated by fractionation (5 mm.) ultimately into two main fractions (i and ii), and a small first fraction consisting essentially of ethyl nonoate. (i) was ethyl *m*-methoxybenzoate (30 c.c.), b. p. 110°/5 mm., 255°/760 mm., $d^{15.5°}$ 1·082, $n_D^{20°}$ 1·491. The liberated acid was identified as *m*-methoxybenzoic, m. p. 106·5° (Found: C, 62·8; H, 5·4; OMe, 20·1; Ag in silver salt, 41·6%). (ii) was ethyl azelate (40 c.c.), b. p. 130—132°/5 mm., 290°/760 mm. The recovered acid, crystallised from water, melted at 106·5° (Found: C, 57·6; H, 8·6; Ag in silver salt, 53·6; acid number, 592. Calc.: C, 57·5; H, 8·5%; acid number, 596).

(b) Campnospermonyl methyl ether (10 g.), dissolved in chloroform (50 c.c.), was treated with ozone in the usual manner, and the small viscous ozonide, after removal of the chloroform in a vacuum, was decomposed by steam. Nonoaldehyde and nonoic and formic acids were readily identified products, the last-named by the usual qualitative reactions and formation of lead formate (Found: Pb, 70·1%). The products not volatile with steam consisted of aldehydic and acid material, non-crystallisable and non-distillable, and obviously complex, consisting apparently of an aromatic nucleus and considerable side chain. No simple aromatic acid or aldehyde appeared to have been formed: this fact, indicative of the absence of complete scission of the molecule at the second ethenoid linkage, together with the production of formic acid was evidence of the presence of the attached methylene group in the chain.

The occurrence of nonoic and azelaic acids as oxidation products demonstrated the presence in campnospermonol of the unsaturated linkage of natural oleic acid.

Reduction Products of Campnospermonol.—(a) Three successive treatments with sodium and alcohol were required to complete the reduction of campnospermonyl methyl ether to the corresponding *secondary alcohol*, $d^{15.5^\circ}$ 0·9191, b. p. 250°/5 mm. (Found: C, 80·9; H, 10·9. $C_{28}H_{46}O_2$ requires C, 81·1; H, 11·1%). The unsaturated linkages remained unaffected.

(b) Pure dry hydrogen was passed into a vigorously shaken solution of campnospermonyl methyl ether (50 g.) in anhydrous ether (200 c.c.) in which 0·25 g. of platinum dioxide was present (Voorhees and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 1397). Saturation was rapid, and *hydrocampnospermonyl methyl ether* was isolated; it crystallised from alcohol in plates, m. p. 54° (Found: C, 80·9; H, 11·4. $C_{28}H_{48}O_2$ requires C, 80·8; H, 11·5%).

The crystalline *oxime* melted at 43° (Found: N, 3·1. $C_{28}H_{49}O_2N$ requires N, 3·2%).

The analytical values indicate addition of four hydrogen atoms to the molecule and the existence in campnospermonol of two ethenoid linkages. By similar reduction of campnospermonyl acetate there was obtained also wax-like *hydrocampnospermonyl acetate* (m. p. 61°; acetyl value 128), sparingly soluble in cold alcohol, from which crystalline *hydrocampnospermonol*, m. p. 70°, was obtained on hydrolysis.

(c) Reduction of campnospermonyl methyl ether with amalgamated zinc and concentrated hydrochloric acid (Clemmensen, *loc. cit.*) proceeded with extreme slowness at 100° even with constant and vigorous agitation. Addition of glacial acetic acid appreciably promoted the reaction. Treatment was continued during several days until, as apparent from the attainment of minimum density of the product, conversion of the carbonyl into the methylene group was complete. The ethenoid linkages were unaffected. The product was a colourless unsaturated *methoxy-hydrocarbon*, almost insoluble in alcohol, $d^{15.5^\circ}$ 0·9093, $n_D^{20^\circ}$ 1·4950, b. p. 226°/5 mm. (Found: C, 84·2; H, 11·6. $C_{28}H_{46}O$ requires C, 84·4; H, 11·6%).

Further reduction with hydrogen in presence of platinum gave a saturated crystalline *methoxy-hydrocarbon*, m. p. 45° (Found: C, 83·2; H, 12·5. $C_{28}H_{50}O$ requires C, 83·6; H, 12·4%), which was stable to permanganate in boiling acetone.

The amount of these methoxy-hydrocarbons available did not permit of further examination.

Oxidation of Hydrocampnospermonyl Methyl Ether.—The reaction between the ether (50 g.) in acetone (200 c.c.) and potassium per-

manganate (157 g.), tardy in the cold, was completed in the boiling solution. After removal of the acetone the manganese dioxide was extracted with (*a*) boiling 90% alcohol and (*b*) boiling water.

(*a*) The potassium salt that separated on concentration and cooling was converted into ethyl ester, b. p. 185°/5 mm., m. p. 28° after recrystallisation. The acid obtained by hydrolysis and recrystallisation from alcohol and from acetone was margaric acid, m. p. 61·5°, acid number 204 (Found: C, 75·3; H, 12·5; Ag in silver salt, 28·8. Calc.: C, 75·5; H, 12·6%; acid number, 207).

(*b*) The aqueous extract, to which was added the mother-liquor from the crystallisation of potassium margarate, was acidified, and the acid extracted by ether was esterified and fractionally distilled. The principal fraction was ethyl *m*-methoxybenzoate with a little ethyl margarate. Oxalic acid was detected in the aqueous extract after removal of the liberated *m*-methoxybenzoic acid.

Reaction of Oximinohydrocampnospermonyl Methyl Ether with Phosphorus Pentachloride.—Hydrocampnospermonyl methyl ether (20 g.), suspended in absolute alcohol (200 c.c.) in which sodium (3 g.) was dissolved, was shaken at 0° with amyl nitrite (15 g.) for several hours. The liquor was then diluted with water, filtered, and treated with acetic acid, an imperfectly crystalline oximino-compound (20 g.), apparently a mixture, being thus obtained. This, in dry chloroform (50 c.c.) at 0°, was treated with phosphorus pentachloride (15 g.) and after several hours the chloroform solution was washed with water and extracted with dilute aqueous potassium hydroxide. The acid yielded by the alkaline solution was converted into an ethyl ester, m. p. 33° after recrystallisation from alcohol; the acid recovered from this was stearic acid, m. p. 69°, acid number 197 (Found: C, 75·8; H, 12·5. Calc.: C, 76·0; H, 12·7%; acid number, 197).

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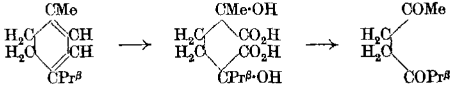
XI.—*Action of Beckmann's Chromic Acid Mixture on Some Monocyclic Terpenes.*

By THOMAS ANDERSON HENRY and HUMPHREY PAGET.

OF the fourteen possible structural isomerides which can be represented by the *p*-menthadiene formula for monocyclic terpenes, eight are known with certainty, four are doubtful, and two are unknown. There are, on the other hand, described in the literature a considerable number of natural hydrocarbons of the formula $C_{10}H_{16}$, the constants of which indicate that they may be *p*-men-

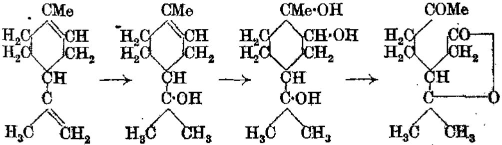
thadienes, but from which crystalline derivatives of the type used for the identification of such terpenes have not been obtained. One of these was the so-called "lævorotatory terpene of chenopodium oil," and in showing that this was composed of a mixture of α-terpinene, *l*-limonene, and *iso*limonene ($\Delta^{2:8(9)}$-*p*-menthadiene) with *p*-cymene, the authors obtained useful confirmatory evidence by examination of the products formed by the gradual oxidation of the mixture with Beckmann's chromic acid mixture (Henry and Paget, J., 1925, **127**, 1649). As a preliminary to that work, a number of the monocyclic terpenes obtainable commercially in a reasonably pure state were oxidised with Beckmann's mixture, and the products examined. As these results, particularly those obtained with α-phellandrene, are of considerable interest and as the method may prove useful in facilitating the identification of terpenes in complex natural mixtures of these products, especially where much *p*-cymene is present, it has been thought desirable to place them on record.

It has already been shown (Henry and Paget, J., 1921, **119**, 1714; 1923, **123**, 1878) that with this oxidising agent α-terpinene (I) is converted mainly into dimethylacetonylacetone (II), only minute quantities of the usual precursor of this diketone, αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid (III), being obtained, even when the reaction is not prolonged. With potassium permanganate, on the contrary, the diketone is formed only in small amounts, the acid in its *anti*- and *para*-forms being the chief product.



(I.) (III.) (II.)

α-Terpinene is readily destroyed; but limonene (IV) is only slowly attacked by Beckmann's mixture, yielding 1 : 2 : 8-trihydroxyterpan (V), m. p. 122°, and the keto-lactone (VI) which Wallach (*Annalen*, 1893, **275**, 153) first obtained by the oxidation of α-terpineol (VII); this, therefore, is probably the product first formed by the action of chromic acid on limonene.



(IV.) (VII.) (V.) (VI.)

The α-phellandrene (VIII) used was purchased on various occasions in London and its botanical origin is unknown, although it was no doubt derived from one or other of the species used for the production of eucalyptus oil. All the samples yielded the same products on oxidation with Beckmann's mixture, *viz.*, thymoquinone and two *ketolactones*, $C_{10}H_{16}O_3$ and $C_9H_{14}O_3$, both of which were isolated in the form of their semicarbazones, which are separable from each other with great difficulty.

The keto-lactone $C_{10}H_{16}O_3$ (IX) is oxidised by sodium hypobromite, but instead of the dibasic hydroxy-acid or its lactone, which would be the normal product, a *dibasic acid*, $C_9H_{14}O_4$, is formed, which is readily oxidised further by potassium permanganate to α-*iso*propylsuccinic acid. Such a dibasic acid may arise from the dibasic hydroxy-acid by loss of water in two ways, to give either β-*iso*propyl-αβ-dihydromuconic acid,

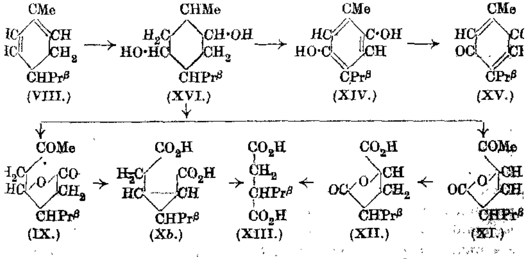
$$CO_2H\cdot CH_2\cdot CHPr^{\beta}\cdot CH{:}CH\cdot CO_2H \ (Xa),$$

which should readily absorb bromine (compare Baeyer and Rupe, *Annalen*, 1890, **256**, 18), or, if carbon atoms 3 and 5 are involved, a *cyclo*propane derivative (X*b*). Oxidation of either could give rise to *iso*propylsuccinic acid, being preceded in the second case by hydration, as in that of dimethyldi*cyclo*pentanonedicarboxylic acid (Farmer and Ingold, J., 1920, **117**, 1369). The molecular refraction of the diethyl ester is closer to that calculated for the unsaturated structure, on the usual assumptions (Eisenlohr, "Spectrochemie organischer Verbindungen," 1912, p. 48), than to that for the *cyclo*propane structure, but as we were unable to form any addition product with bromine the cyclic formula cannot be left out of account.

The second keto-lactone, $C_9H_{14}O_3$, we propose to represent by formula (XI). It furnishes with sodium hypobromite bromoform and a lactone acid, $C_8H_{12}O_4$ (XII), which on further oxidation by permanganate yields α-*iso*propylsuccinic acid (XIII). The latter also occurs, as would be expected, among the direct oxidation products of α-phellandrene by Beckmann's mixture, and it has already been obtained by Semmler (along with α-*iso*propylglutaric acid: the latter being attributed to the presence of β-phellandrene) by the oxidation of commercial phellandrene from eucalyptus oil with permanganate (*Ber.*, 1903, **36**, 1749). Semmler's acid had m. p. 116°, was optically active, although no specific rotation is quoted, and gave an anilic acid, m. p. 143°; the melting point of the racemic anilic acid has been given as 145° (Bentley, Perkin, and Thorpe, J., 1896, **69**, 274), 139° (Bone and Sprankling, J., 1900, **77**, 658), and 135° (Crossley, J., 1902, **81**, 682). The acid we have obtained has m. p. 95°, $[\alpha]_D$ − 22·64° (sodium salt), and yields a

anilic acid, m. p. 129°. Apart from an observation by Wallach (*Annalen*, 1900, **313**, 354), who gives 85—88°, no melting point lower than 115° seems to have been recorded previously for α-*iso*-propylsuccinic acid, and we at first thought our acid must be *l*-α-*iso*propylglutaric acid, for which m. p.'s 92° to 97° have been recorded and from which on one occasion Wallach prepared an anilic acid, $[\alpha]_D - 24.2°$, m. p. 129° (*Annalen*, 1911, **379**, 189), although this derivative is stated by Semmler (*loc. cit.*) to melt at 159°. To make sure of this point, we resolved *dl*-α-*iso*propyl-succinic acid into its optical antipodes. The two optically active forms obtained melted at 94°, and had $[\alpha]_D \pm 23°$ (approx.). The anilic acid of the *d*-form had m. p. 129°. Mixtures of our acid with (*a*) the *d*-form and (*b*) the *l*-form melted at 117° and 94°, respectively, and a mixture of our anilic acid with that from the *d*-acid at 142°. There can be no doubt, therefore, that the acid produced directly and indirectly by the oxidation of *l*-α-phellandrene is *l*-α-*iso*propylsuccinic acid. In addition, a small quantity of the racemic acid was obtained, probably due to some racemisation of the *l*-phellandrene.

In view of these facts, it seems possible that occasionally α-*iso*-propylsuccinic acid has been mistaken for α-*iso*propylglutaric acid. Thus in Wallach's case (*loc. cit.*) the original acid melted at 92—93° and had $[\alpha]_D - 15.82°$, but on treatment of its anhydride with aniline it yielded two anilic acids, melting at 153—155° and 129°, respectively. Only the former was analysed and gave good results for *iso*propylglutaranilic acid. The second anilic acid had $[\alpha]_D -$ 24.2°, and it seems quite likely that it was α-*iso*propylsuccinanilic acid and that the acid, m. p. 92—93°, was a mixture.



There is also formed from α-phellandrene, in addition to these acids, thymoquinol (XIV) and thymoquinone (XV). The latter

has been found to form a disemicarbazide derivative in addition to the hydroxymethyl*iso*propylbenzeneazoformamide described by Heilbron and Henderson (J., 1913, **103**, 1419).

The ultimate residue of unattacked oil is a mixture of cineole, which is a natural constituent of the oil from which the α-phellandrene was prepared, and *p*-cymene, which is also known to occur in the essential oils of the eucalyptus species (see Baker and Smith, "Eucalypts and their Essential Oils," 1920, p. 356); the latter was identified by analysis and by oxidation to *p*-hydroxy*iso*propylbenzoic acid.

That *p*-cymene was actually present in the commercial phellandrene used, was proved by removing the phellandrene as the nitrosite and the cineole as the resorcinol compound and examining the residual oil; it was then found that about 17% of the original material consisted of this hydrocarbon. *p*-Cymene is attacked exceedingly slowly by Beckmann's chromic acid mixture, yielding *p*-methylacetophenone in minute quantities.

All the oxidation products of α-phellandrene now described may be regarded as derived from a primary dihydric cyclic alcohol (XVI) produced by the addition of the elements of a molecule of water at each of the ethylenic linkages of α-phellandrene (VIII).

It is probable that this is also the chief mode of attack of the reagent on α-terpinene (I), since dimethylacetonylacetone (II) is the normal product and only minute quantities of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid have been found, for the formation of which it is necessary to assume (Wallach, *Annalen*, 1908, **362**, 296) the addition of a hydroxyl group at each end of each of the ethylenic linkages. On the contrary, the production of 1 : 2 : 8-trihydroxyterpan (V) from limonene (IV) requires the hydration of the extracyclic ethylenic linkage to form terpineol (VII) and the subsequent addition of a hydroxyl group at each end of the cyclic double linkage to form the trihydric alcohol (V).

EXPERIMENTAL.

In the earlier experiments, 100 c.c. of the terpene under examination were shaken repeatedly with an equal volume of Beckmann's mixture until no further absorption of the terpene took place, but it was subsequently found more convenient to treat the terpene with 20 times its volume of the oxidising agent, and to submit the recovered oil to a second treatment as soon as enough had been accumulated for this purpose. Both processes yielded the same products. The unattacked oil (D) was separated from the chromic acid liquor and the latter was thoroughly extracted with ether free from alcohol. On removal of the solvent, a viscid oil was left,

which was redissolved in sufficient ether and separated into acid (B) and neutral (A) portions by repeated agitation with a saturated aqueous solution of sodium carbonate. A further quantity of acid (C) was usually obtained by concentrating the chromic acid liquor after neutralisation, again making it acid and extracting it with ether.

Limonene.

Limonene is much less readily attacked by Beckmann's mixture than phellandrene, but oxidation proceeds a little more rapidly if the terpene is diluted with an equal volume of glacial acetic acid.

Limonene ($d_{16^\circ}^{16^\circ}$ 0·8484, $[\alpha]_D^{16^\circ}+90{\cdot}1^\circ$) (50 c.c.), dissolved in glacial acetic acid (50 c.c.), was shaken mechanically for 5 days with 1000 c.c. of Beckmann's mixture. The unattacked terpene was then separated (46 c.c.) and the products were treated as described above; after 14 repetitions of the process, 8 c.c. of oil remained, $[\alpha]_D^{16^\circ}+48{\cdot}5^\circ$. The neutral extract (A) (28 g.), after distillation, yielded a *semicarbazone* which crystallised from alcohol in minute needles, m. p. 210°, $[\alpha]_D^{18^\circ}+1{\cdot}28^\circ$ in acetic acid ($c=$ 1·486) (Found: C, 54·4; H, 8·0; N, 18·1. $C_{11}H_{19}O_3N_3$ requires C, 54·8; H, 7·9; N, 17·4%). This was proved by a mixed melting-point determination to be identical with the semicarbazone of the keto-lactone, $C_{10}H_{16}O_3$, obtained by the oxidation of α-terpineol. The keto-lactone, recovered as described (p. 76), had m. p. 58—60°; $[\alpha]_D^{18^\circ}-2{\cdot}12^\circ$ in water ($c=1{\cdot}552$) and $-7{\cdot}87^\circ$ in benzene ($c=2{\cdot}008$) (Found: 1 g. equiv. to 5·31 c.c. of *N*-sodium hydroxide. Calc. for $C_{10}H_{16}O_3$, 5·4 c.c.).

The residue from the distillation of the crude extract deposited on standing a small amount of a neutral crystalline substance, insoluble in ether, with which it was well washed; it then melted at 121°, alone or mixed with a specimen of 1:2:8-trihydroxy-terpan, $C_{10}H_{20}O_3$, prepared from α-terpineol by oxidation with potassium permanganate as described by Wallach (*Annalen*, 1893, 275, 153).

α-Phellandrene.

The four supplies of commercial α-phellandrene used had the following constants: $d_{16^\circ}^{16^\circ}$ 0·8525, $[\alpha]_D^{16^\circ}-98{\cdot}5^\circ$; $d_{16^\circ}^{16^\circ}$ 0·8519, $[\alpha]_D^{18^\circ}-67{\cdot}7^\circ$; $d_{16^\circ}^{16^\circ}$ 0·8828, $[\alpha]_D^{18^\circ}-56{\cdot}1^\circ$; $d_{20^\circ}^{20^\circ}$ 0·8531, $[\alpha]_D^{20^\circ}-75{\cdot}0^\circ$.

From 1 litre of terpene the average yields of the four crude oxidation products referred to above were (A) 110 g.; (B) 102 g.; (C) 28 g.; (D) 590 g.

Extract A (Neutral Oil).—This on treatment with semicarbazide acetate in alcohol yielded immediately a *semicarbazone*, crystallising in colourless, glistening leaflets, but all attempts to isolate the

original carbonyl compound from the crude extract by direct or steam distillation, or by the use of sodium hydrogen sulphite solution, failed. The total extract was therefore treated with excess of semicarbazide solution, and the mixture left for about 12 hours. The product was recrystallised until of constant melting point, 187° (corr.), from hot 95% alcohol. It had $[\alpha]_D^{20°}$ + 28·9° (c = 0·26 in alcohol or 1·96 in acetic acid), + 11·27° (c = 1·61 in alcoholic sodium ethoxide), or + 4·13° (c = 1·6 in aqueous sodium hydroxide) (Found for substance dried in a vacuum at 105°: C, 52·65; H, 7·7; N, 18·75. $C_{10}H_{17}O_3N_3$ requires C, 52·9; H, 7·5; N, 18·5%).

The semicarbazone was hydrolysed by 15% hydrochloric acid in presence of ether, the ethereal solution washed with sodium carbonate solution and dried over anhydrous sodium sulphate, and the solvent distilled off, leaving a colourless oil, which crystallised. It had m. p. 48—50°, $[\alpha]_D^{20°}$ + 37·1° in water (c = 1·67) and —43·13° in benzene (c = 1·46) (Found: C, 63·4; H, 8·4. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%). An aqueous solution of the substance remains neutral for several days, but such solutions neutralise caustic alkalis and 6·1 c.c. of N-sodium hydroxide were necessary to neutralise 1 g. of the substance. The amount of alkali required to convert a keto-lactone $C_9H_{14}O_3$ into the corresponding ketohydroxy-acid, $C_9H_{16}O_4$, is 5·9 c.c. Attempts to isolate the acid from solutions of the sodium salt by addition of weak acids and extraction with solvents merely led to the regeneration of the original keto-lactone.

The keto-lactone (0·9 g.), dissolved in the calculated quantity of N-sodium hydroxide, was treated with a 4% solution of potassium permanganate until decolorisation no longer took place rapidly. The oil (0·8 g.) extracted from the acidified liquor by ether had a strong odour of acetic acid and crystallised on standing. The crystals had m. p. 93—95°, alone or mixed with *l-iso*propylsuccinic acid prepared as described below; admixture with *d-iso*propylsuccinic acid raised the melting point to 110—117°.

When the keto-lactone (3 g.), dissolved in the calculated quantity of aqueous sodium hydroxide, was added to excess of a freshly-prepared, ice-cold solution of sodium hypobromite, the mixture became cloudy and deposited bromoform. After 1 hour, the latter was extracted with ether and the aqueous liquor was freed from hypobromite by cautious addition of sodium hydrogen sulphite, acidified, and again extracted with ether. This removed an oil (2·3 g.), which on careful trituration with dry benzene deposited a crystalline substance, m. p. 225° (decomp.), which contained 31% of bromine but could not be obtained in sufficient quantity for

detailed examination. The bulk of the acid was evidently a lactonic acid, since 1 g. required 6·15 c.c. of *N*-sodium hydroxide for neutralisation in the cold and 10·74 c.c. when heated with the alkali ($C_8H_{12}O_4$ requires 5·8 c.c. of *N*-sodium hydroxide for neutralisation of one carboxyl group and 11·65 c.c. for conversion into the corresponding hydroxy-dicarboxylic acid $C_8H_{14}O_5$). The *silver* salt prepared from the disodium salt contained Ag, 53·6% (Calc. for $C_8H_{12}O_5Ag_2$: Ag, 53·4%) (Found for *lead* salt : C, 24·9; H, 3·7; Pb, 52·3. $C_8H_{12}O_5Pb$ requires C, 24·3; H, 3·0; Pb, 52·4%).

On regeneration from the lead salt by treatment with dilute sulphuric acid and extraction with ether, the original lactonic acid was obtained as an oil, which slowly solidified when kept in a vacuous desiccator; it then melted at 58—60° (Found : C, 55·75; H, 7·0. $C_8H_{12}O_4$ requires C, 55·9; H, 7·0%).

On further oxidation with potassium permanganate, this lactonic acid, $C_8H_{12}O_4$, was converted into *l-iso*propylsuccinic acid, which was isolated and identified as described above (p. 76).

This stage of the oxidation of α*-phellandrene is represented by* formulæ VIII, XVI, XI, XII and XIII (p. 73).

On keeping the liquors from which the semicarbazone, m. p. 187°, was separated, for 2—3 days, a second semicarbazone was obtained the yield of which varied from a mere trace to as much as 20%. It crystallised from alcohol in small, colourless needles, m. p. 183°, $[\alpha]_D^{21°}$ + 55·47° in acetic acid (c = 2·08) (Found : C, 54·8; H, 8·0; N, 17·8. $C_{11}H_{19}O_3N_3$ requires C, 54·8; H, 7·9; N, 17·4%). A mixture with the first semicarbazone melted at 168—174°. The solubility of these two semicarbazones in alcohol is about the same, 0·2% at 15°; a mixture of the two is more soluble and very difficult to separate.

The carbonyl compound was obtained from the semicarbazone by the method already described (p. 76). It did not crystallise but distilled unchanged at 155—160°/1 mm.; $[\alpha]_D^{20°}$ + 73·67° in water (c = 1·775) and + 54·79° in benzene (c = 1·566) (Found : C, 65·1; H, 9·0. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·7%). It dissolves to a neutral solution in water, but this solution neutralises sodium hydroxide, 1 g. of the substance requiring 5·36 c.c. of *N*-sodium hydroxide ($C_{10}H_{16}O_3$ requires 5·44 c.c. for conversion into the ketohydroxy-acid, $C_{10}H_{18}O_4$). The substance is therefore a *keto-lactone*, $C_{10}H_{16}O_3$.

When this keto-lactone (1·7 g.) was oxidised with alkaline hypobromite as described above, bromoform was produced and an almost quantitative yield (1·5 g.) was obtained of an *acid* which after recrystallisation from benzene melted constantly at 138° and had $[\alpha]_D^{19°}$ + 15·99° in aqueous sodium hydroxide (c = 4·196). It was

readily soluble in alcohol or ether, sparingly soluble in water. It gave no *evidence of a lactone* structure (Found: C, 58·0; H, 7·6. 1 G. was equiv. to 10·58 c.c. of *N*-sodium hydroxide. Found in the *silver* salt: Ag, 53·6. $C_9H_{14}O_4$ requires C, 58·1; H, 7·6%. 1 G. is equiv. to 10·74 c.c. of *N*-sodium hydroxide. $C_9H_{12}O_4Ag_2$ requires Ag, 53·95%). The diethyl ester distilled at 168—170°/17 mm. and had $d_{19°}^{19°}$ 1·0046, $[\alpha]_D^{18°}$ + 18·05° in alcohol (c = 7·26), $n_D^{20°}$ 1·4530, whence $[R_L]_D$ = 65·15 (Found: C, 64·1; H, 9·25. $C_{13}H_{22}O_4$ requires C, 64·5; H, 9·1%). The calculated molecular refraction for a diethyl ester of this empirical formula is 63·11, to which must be added 1·73 for an ethylenic linkage or 0·7 for a *cyclo*propane structure, making 64·84 and 63·81, respectively. It was therefore a dicarboxylic acid and appeared not to contain an ethylenic linkage, since on treatment with bromine in solvents no addition took place and the acid was recovered unchanged; the ester behaved similarly. The acid was readily oxidised by an aqueous solution of potassium permanganate at 0°, yielding an *acid which slowly crystallised* in plates, m. p. 95°, and showed no depression of melting point when mixed with *l*-*iso*propylsuccinic acid, but raised that of the *d*-acid to 113—117°. This stage of the oxidation of α-phellandrene is represented by formulæ VIII, XVI, IX, X*a* or X*b*, XIII (p. 73).

Extracts B *and* C.—The acid extracts did not crystallise on standing; an insoluble lead salt was obtained by addition of lead acetate to an aqueous solution of the acids, previously neutralised by sodium hydroxide. The acid recovered from this lead salt crystallised from water, in which it was very soluble, in plates, m. p. 95°; $[\alpha]_D^{18°}$ − 22·64° in water (c = 8·80) [Found: C, 52·9; H, 7·7. 1 G. was equiv. to 11·8 c.c. of *N*-sodium hydroxide. $C_5H_{10}(CO_2H)_2$ requires C, 52·5; H, 7·5%. 1 G. is equiv. to 12·5 c.c. of *N*-sodium hydroxide]. The anhydride distilled at 140—150°/15 mm., and with aniline in benzene solution gave an *anilic acid* crystallising from benzene in leaflets, m. p. 129° (Found: N, 6·1. $C_{13}H_{17}O_3N$ requires N, 5·9%). *dl*-*iso*Propylsuccinic acid melts at 117° and its anilic acid at 144°, and admixture of these substances caused no depression of melting point below those of the acid and anilic acid, respectively, from phellandrene, which therefore appeared to be *l*-*iso*propylsuccinic acid and its anilic acid. Since some confusion exists as to the physical constants of the optically active forms of this acid (see p. 73), and it appears unlikely that it has previously been obtained in a pure state, a specimen of the *dl*-acid, m. p. 117°, $[\alpha]_D$ ± 0°, the remainder of a sample received from the late Prof. A. W. Crossley, was resolved. The *quinine* salt crystallised well from alcohol, the less soluble salt (m. p. 206° $[\alpha]_D^{25°}$ − 125·4°) yielding an acid, m. p. 93—105°, $[\alpha]_D^{20°}$ + 12·1°

The *quinidine* salt also crystallised well, but, like the quinine salt, only furnished a partly deracemised acid. The *strychnine* salt separated from alcohol in long needles. On drying in a vacuum at 100°, or on boiling with alcohol, this salt partly dissociated and free strychnine was obtained as a first crop, $[\alpha]_D^{25°}$ − 140·9° in chloroform (c = 1·884). The second crop also contained free strychnine, and no accurate constants could be obtained for the salt. From the second and other early fractions, however, an acid was recovered, m. p. 94°, $[\alpha]_D^{20°}$ + 22·99° in water (c = 5·64). When no more of the sparingly soluble strychnine salt could be induced to separate, the acid was recovered from the residues and converted into the *brucine* salt, which crystallised well from acetone; m. p. 144° (decomp.), $[\alpha]_D^{20°}$ − 15·9° in chloroform (c = 1·929). The acid recovered from this melted at 94° and had $[\alpha]_D^{20°}$ − 23·46° in water (c = 12·866). This *l*-acid showed no depression of melting point when mixed with the *l*-acid, $C_7H_{12}O_4$, obtained directly (p. 78) and indirectly (p. 76) from phellandrene; admixture with the *d*-acid raised the melting point to 115—117°, and this was not depressed by further addition of the *dl*-acid. The anilic acid prepared from the anhydride of the *d*-acid obtained by distillation melted at 129°, and a mixture of this with the anilic acid of the *l*-acid from phellandrene at 142—144°.

The remainder of the extracts B and C consisted of oily acids from which no well-defined product could be isolated, either by fractional precipitation with metallic salts or by fractional distillation of the ethyl or methyl esters.

Recovered Oil (D).—The colour of the unoxidised oil varied from pale yellow to dark brown. It was separated by distillation into four fractions: (1) b.p. 70°/25 mm. or 172—180°/760 mm. (60%); (2) b. p. 70—110°/25 mm. (25%); (3) b. p. 115—120°/25 mm. (8%); and (4) a black, tarry residue, distilling with decomposition at 200°/15 mm. (7%).

Fraction (1) had a strong odour of cineole, due, no douht, to the presence of this substance in the phellandrene used, and cineole equivalent to 8% by weight of extract D was isolated from it by repeated agitation with a 50% solution of resorcinol. The residue of fraction (1), after removal of cineole and repeated distillation over metallic sodium, had b. p. 176—180°/760 mm., $[\alpha]_D \pm 0°$, and consisted principally of *p*-cymene, identified by oxidation to hydroxy-*iso*propylbenzoic acid, m. p. 157°, with a hot aqueous solution of potassium permanganate. The yield of *p*-cymene amounted to about 25% of the α-phellandrene used. An attempt to estimate the amount of *p*-cymene originally present was made by removing the phellandrene as nitrosite in the way described by Smith, Hurst,

and Read (J., 1923, **123**, 1663). The petroleum solution from which the nitrosite was removed was again treated with nitrous acid, and the residual oil then shaken three times, for several hours at a time, with a 50% solution of resorcinol in water, and finally repeatedly distilled over sodium at 176—178°/760 mm. The amount of *p*-cymene remaining was 17% (Found: C, 89·5; H, 10·5. Calc.: C, 89·55; H, 10·45%).

Fractions (2) and (3) were bright yellow to brown and on standing for some time with an alcoholic solution of semicarbazide acetate deposited either yellow crystals, or colourless crystals which rapidly became yellow on exposure to light. Both forms melted at temperatures varying from 224° to 237° and on recrystallisation from boiling acetic acid gave bright yellow fractions melting constantly at 237°; a second yellow crystalline substance, which melted constantly at 204°, accumulated in the acetic acid mother-liquors. A similar but less complete separation can be effected by boiling alcohol, in which the substance melting at 237° is much less soluble than in acetic acid, but treatment with boiling alcohol leave undissolved a minute amount of a pale yellow substance, m. p. 257°

The substance melting at 204° appears to be the 4-hydroxy 3-methyl-5-*iso*propylbenzeneazoformamide of Heilbron and Hender son (*loc. cit.*) formed by the interaction of thymoquinone with on molecule of semicarbazide. It separates from acetic acid in brigh red crystals, which rapidly effloresce and become yellow, losing tw molecules of acetic acid on exposure at room temperature. Drie at 100° in a vacuum, it lost 35·5% ($C_{11}H_{15}O_2N_3$, $2C_2H_4O_2$ require loss, 35·2%) (Found: C, 59·6; H, 6·9; N, 19·0. $C_{11}H_{15}O_2N$ requires C, 59·7; H, 6·8; N, 19·0%).

The yellow and the white substance melting at 237° appear to b two forms of *thymoquinone disemicarbazone* (Found: C, 51·[illegible] H, 6·8; N, 29·9. $C_{12}H_{18}O_2N_6$ requires C, 51·8; H, 6·5; N, 30·2% This has never been prepared previously, but can readily be obtaine by the action of excess of semicarbazide acetate on thymoquinon dissolved in cymene or any other solvent which will retard reacti between the two components, or by prolonged ebullition of thym quinone with excess of semicarbazide in alcohol. Under the conditions, the yellow form, m. p. 237°, alone is produced (Foun N, 29·9%). We have been unable to determine the conditio which will lead with certainty to the production of the labile wh form, but once it is produced it can be preserved by washing it wi cold acetic acid and storing it in the dark. On recrystallisati from boiling acetic acid, both this colourless form and the substan melting at 257° pass into the yellow modification, m. p. 237°.

Fraction (4), on long standing and careful trituration with eth

deposited a small amount of a colourless, crystalline substance, m. p. 142°, which proved to be thymoquinol, since it showed no depression of melting point when mixed with thymoquinol prepared by reduction of thymoquinone with titanous chloride (Found: C, 72·1; H, 8·7. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·4%).

The remainder of fractions (2), (3), and (4) consisted of oily and tarry substances from which no well-defined products could be isolated.

The authors are indebted to Mr. E. M. Gibbs for much assistance in the experimental work.

WELLCOME CHEMICAL RESEARCH LABORATORIES.
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XII.—*The Cyanine Dyes. Part X. The Constitution of the* apo*Cyanines.*

By WILLIAM HOBSON MILLS and HENRY GEOFFREY ORDISH.

THE action of alcoholic potash on a mixture of a quinoline alkyl-iodide and a quinaldine alkyliodide leads, as is well known, to the formation of an *iso*cyanine. Very similar dyes, the *apo*cyanines, are, however, formed by the action of alcoholic potash on a quinoline alkyliodide alone (D.R.-P., 154448). In this condensation, two molecules of quinoline alkyliodide condense with the loss of the elements of one molecule of hydrogen iodide, and two isomeric dyes, one yellow—the xantho*apo*cyanine—and the other red—the erythro*apo*cyanine—result. On the probable assumption that the alkyl groups remain intact, the reaction may be represented as follows:

$$2(C_9H_7NR)I - HI = (C_{18}H_{13}N_2R_2)I,$$

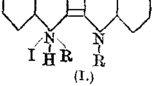
where R represents the alkyl group.

These compounds were investigated by Kaufmann and Strübin (*Ber.*, 1911, **44**, 690), who suggested formula (I) for the erythro-*apo*cyanines. This, however, cannot be regarded as a satisfactory representation of these compounds, as it accords neither with their intense colour nor with their stability towards alkalis. We have therefore undertaken an investigation of these dyes and have selected the erythro*apo*cyanine derived from quinoline ethiodide for this purpose, as it is formed in better yield and, on account of its greater solubility, is more easily handled than the isomeric xantho*apo*cyanine.

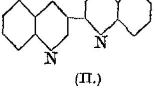
We first tried the method of oxidation with potassium permanganate which had proved successful in fixing the constitution of the *iso*cyanines (Mills and Wishart, J., 1920, **117**, 579). The chief product was a diquaternary ammonium compound, which was isolated as a dichromate, and the corresponding iodide proved to be identical with the iodide obtained by Kaufmann and Strübin by oxidising the *apo*cyanine with iodine. This oxidation, which was effected smoothly either by potassium permanganate or by iodine, brought about the removal of one hydrogen atom per molecule and the addition of an equivalent of an acid radical:

$$(C_{18}H_{13}N_2Et_2)I + I_2 = (C_{18}H_{12}N_2Et_2)I_2 + HI.$$

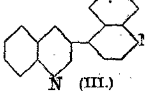
The nature of this product was easily inferred, for its composition and molecular weight, considered together with its ultimate origin from quinoline ethiodide, indicated that it was the diethiodide of a diquinolyl, $C_{18}H_{12}N_2$. Further, by heating the corresponding *diethochloride* in a vacuum, two molecules of ethyl chloride were eliminated and the diquinolyl itself was isolated. *Ethylerythro-apocyanine* so clearly resembles the other classes of cyanine dyes that it seemed certain that its colour must be due to an analogous canse. It must consequently be associated with the presence of two NEt groups, in one of which the nitrogen is in the ammonium form, and in the other tervalent, connected by a chain of conjugated linkages In order that the two nitrogen atoms may have this different function there must necessarily be an odd number of carbon atoms in the connecting chain. The molecules of the diquinolyl dieth iodide and the erythro*apo*cyanine, being so readily interconvertibl by the simple elimination or introduction of a hydrogen atom witl the addition or removal of an ionic charge, must have the sam carbon skeleton. The diethiodide must therefore be derived fron a diquinolyl in which the two nitrogen atoms are separated b an odd number of carbon atoms. This condition is satisfied b the diquinolyls (II) and (III), in which the 3-position of on nucleus is linked to the 2- and to the 4-position respectively of th other.



(I.)



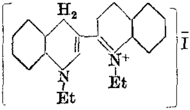
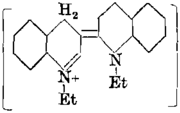
(II.)

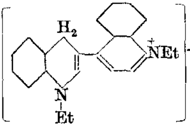
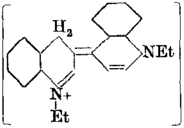


(III.)

The probability that the *apo*cyanines are derived from a 3-quinoly quinoline is increased when it is remembered that the diquinol

most easily prepared (by heating quinoline with sodium; Weidel, *Monatsh.*, 1881, 2, 491) has been shown to have the constitution (II) (Carlier and Einhorn, *Ber.*, 1890, 23, 2895). From diethiodides of diquinolyls of this constitution, the dyes will be obtained by the addition of one atom of hydrogen and the removal of one atom of iodine per molecule. There is only one possible position for the added hydrogen, which will leave a conjugated chain of unsaturated linkages between the two nitrogen atoms; namely the 4-position. These conditions, therefore, lead to the view that the *apo*cyanines are to be represented by the following formulæ:

(IV.)  or  (V.)

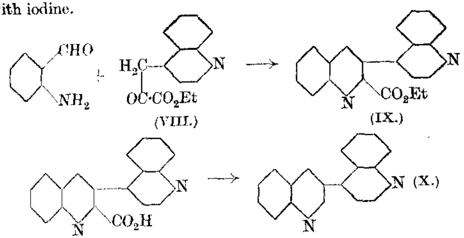
(VI.)  or  (VII.)

If these conclusions are correct, the tautomeric formulæ (IV) and (V), having a conjugated chain of three carbon atoms, represent the xantho*apo*cyanine, and the formulæ (VI) and (VII), with the longer chain of five atoms (as in the *iso*cyanines), represent the more deeply coloured red erythro*apo*cyanine.

Formulæ corresponding with (V) and (VII) were proposed by König five years ago (*Ber.*, 1922, 55, 3293), but without proof. In the present paper, an experimental demonstration is given that the erythro*apo*cyanine has a constitution shown by formula (VI) (or VII). This was effected by synthesising the diquinolyl (III), and showing that its diethiodide was identical with that obtained by oxidising the dye with iodine.

This synthesis was carried out in the following manner. Ethyl 4-quinolylpyruvate (lepidineoxalate) (VIII) (Wislicenus, *Ber.*, 1909, 42, 1141) was heated with *o*-aminobenzaldehyde, two molecules of water being eliminated and *ethyl* 3 : 4′-*diquinolyl*-2-*carboxylate* (IX) formed, a synthesis of the Friedländer type having evidently occurred. The corresponding *acid* lost carbon dioxide on heating, giving the 3 : 4′-diquinolyl (X), and the diethiodide of this was

found to be identical with that obtained from the dye by oxidation with iodine.



By means of a similar series of reactions starting with ethyl 2-quinolylpyruvate and *o*-aminobenzaldehyde we have synthesised the 2 : 3′-*diquinolyl, which is identical with* that obtained by heating quinoline with sodium. A proof of the constitution of this diquinolyl is thus afforded which confirms that given by Carlier and Einhorn (*loc. cit.*).

EXPERIMENTAL.

*Diethylerythro*apo*cyanine Iodide.*—For the preparation of this compound we followed closely the details given in D.R.-P. (*loc. cit.*) Pure quinoline ethiodide (14 g.) was dissolved in the smallest possible quantity of boiling methyl alcohol, and two equal volumes (each of 7 c.c.) of a 10% solution of potassium hydroxide in methyl alcohol were added, one at the beginning and the other after an interval of about 10 minutes. The mixture was boiled for about 4 hours and, after dilution with methyl alcohol (50 c.c.), allowed to stand over-night. Crystals of both the erythro- and the xantho-*apo*cyanine were deposited (yield, about 30%), and separation was effected by recrystallisation from ethyl alcohol, in which the xantho-*apo*cyanine is the less soluble. A further small quantity of the mixed dyes could be obtained by evaporating the mother-liquor to two-thirds of the original bulk. The diethylerythro*apo*cyanine iodide formed reddish-brown needles with a green reflex. The analogous xantho*apo*cyanine was obtained as an orange, crystalline powder in a yield of 5%.

*Oxidation of Erythro*apo*cyanine Chloride.*—An aqueous solution of erythro*apo*cyanine chloride, prepared from the corresponding iodide (2 g.) by the action of silver chloride, was diluted with water (to 100 c.c.) and cooled to 0°, and a 2% solution of potassium permanganate added drop by drop to the well-stirred solution. The clear filtrate was extracted twice with chloroform and evaporated

dryness, and the residue extracted with absolute alcohol. The oil obtained on evaporation of the alcohol yielded a crystalline dichromate, m. p. 211°, having a composition the same as that of the dichromate obtained by Kaufmann and Strübin by the direct oxidation of the dye with sodium dichromate (Found: Cr, 19·1. Calc. for $C_{22}H_{22}O_7N_2Cr_2$: Cr, 19·0%). The dichromate obtained as described by Kaufmann and Strübin (*loc. cit.*) gave Cr, 19·1%.

3 : 4′-*Diquinolyl-2-carboxylic Acid.*—Ethyl 4-quinolylpyruvate (4·6 g.) was mixed with *o*-aminobenzaldehyde (2·4 g.) and heated in a vacuum (12—15 mm.) at 150—160° until water vapour ceased to be evolved. The dark-coloured product, consisting of the crude ethyl diquinolylcarboxylate, was dissolved in alcohol and hydrolysed by warming with an excess of 10% aqueous sodium hydroxide. The solution of the resulting sodium salt was extracted twice with ether to remove impurities, filtered, and made acid with acetic acid. 3 : 4′-*Diquinolyl-2-carboxylic acid* separated on standing as a brown, crystalline deposit which was purified by boiling in alcohol with animal charcoal. The pure acid was obtained as a colourless, crystalline powder from alcohol, or as prisms containing 1½ molecules of water from 30% acetic acid (Found: H_2O, 8·4. $C_{19}H_{12}O_2N_2,1\frac{1}{2}H_2O$ requires H_2O, 8·3%). The anhydrous acid melts and decomposes at 204° (Found: C, 75·9; H, 3·9. $C_{19}H_{12}O_2N_2$ requires C, 76·0; H, 4·0%).

3 : 4′-*Diquinolyl.*—By heating 3 : 4′-diquinolyl-2-carboxylic acid to 205° carbon dioxide was eliminated; the impure diquinolyl, after being washed with sodium carbonate solution, was obtained as a white, apparently amorphous powder by allowing its solution in light petroleum to evaporate slowly; m. p. 83—84° (Found: C, 84·3; H, 4·7; N, 10·0. $C_{18}H_{12}N_2$ requires C, 84·4; H, 4·7; N, 10·9%). A crystalline *picrate* was prepared, m. p. 243°.

Preparation of 3 : 4′-*Diquinolyl from Erythro*apo*cyanine Iodide.*—The diethiodide, obtained by oxidising the dye with iodine as described by Kaufmann and Strübin (*loc. cit.*), was converted by silver chloride into the corresponding water-soluble diethochloride deliquescent crystals, m. p. 121°). By heating this compound in a vacuum (1—2 mm.), ethyl chloride was removed and a dark red sublimate formed in the cooler parts of the tube. This was extracted with benzene and yielded a white powder, which, like the synthetic product, could not be induced to crystallise. It gave, however, the same crystalline picrate, m. p. 244°, mixed m. p. 244°, and could also be converted into the original diethiodide, m. p. 198°, mixed m. p. 198°.

3 : 4′-*Diquinolyl Diethiodide.*—3 : 4′-Diquinolyl was boiled with an excess of ethyl iodide for 4 hours, and the resulting solid was recrystallised from dilute alcohol, giving the pure salt as orange-

yellow crystals, m. p. 198° (Found: I, 44·9. $C_{22}H_{22}N_2I_2$ requires I, 44·7%). This compound was identical with that prepared directly from the dye by oxidation with iodine as described by Kaufmann and Strübin. There was exact correspondence in the appearance and behaviour of these two products in the melting-point tube; moreover the synthetical product did not dissolve in a saturated solution of the other.

2′ : 3-*Diquinolyl-2-carboxylic Acid.*—Ethyl 2-quinolylpyruvate (Wislicenus, *loc. cit.*) (4·8 g.) and *o*-aminobenzaldehyde (2·4 g.) were dissolved in 50% alcohol (15 c.c.), 10% potassium hydroxide solution (30 c.c.) was added, and the mixture kept for 24 hours. An excess of alkali was then added and the whole steam-distilled to remove any unchanged *o*-aminobenzaldehyde and quinaldine. The residue, after filtration, was made almost neutral with hydrochloric acid, and an excess of acetic acid added. The diquinolylcarboxylic acid separated as a very sparingly soluble, brown powder this was precipitated from boiling glacial acetic acid by water as a white powder, m. p. 175° (decomp.) (Found: C, 75·8; H, 4·2 $C_{19}H_{12}O_2N_2$ requires C, 76·0; H, 4·0%).

2′ : 3-*Diquinolyl.*—When 2′ : 3-diquinolylcarboxylic acid wa heated to 175°, carbon dioxide was given off. The residue crystallised from alcohol or benzene in small, colourless prisms, m. p. 175°

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XIII.—*Stereoisomerism of Disulphoxides and Relate Substances. Part II. Derivatives of* 1 : 4-*Dithian.*

By ERNEST VERE BELL and GEORGE MACDONALD BENNETT.

A DETAILED study of the reactions of the two dithian dioxid recently described (J., 1927, 1798) has provided further eviden that they are stereoisomeric. The two substances behave in almost identical manner with a series of reagents. Each yields *hydrochloride* (compare Fromm, *Annalen*, 1913, **396**, 75) and unstable *hydrobromide*. Each is at once reduced by hydriodic ac and by phosphorus pentachloride, the latter reaction being hig exothermic. They yield crystalline *mercurichlorides* (compare t mercurichloride of a sulphoxide described by Zincke and Frohnebe *Ber.*, 1909, **42**, 2729) and *bromides* sparingly soluble in water.

No compound of a sulphoxide with bromine has been descrit

hitherto, yet there is no difficulty in formulating such a substance. The dibromide of a monosulphoxide might have either of the structures $\underbrace{R_2\overset{+}{S}\text{–}O\text{–}Br}_{\bar{\text{Br}}}$ and $\underbrace{R_2\overset{+}{S}<^{\bar{O}}_{\underset{+}{Br}}}_{\bar{\text{Br}}}$, of which the former is perhaps the more probable (compare the case of dimethiodide formation, Bennett and Hock, J., 1927, 2496). With either structure, the conversion of the $\bar{Br}$ ion into the $\bar{Br}_3$ ion is to be expected in the presence of a large excess of bromine. A partial study of the system water–α-dithian dioxide–bromine shows the existence of a *tetrabromide* and a *hexabromide*. This is in agreement with the considerations advanced above.

The structure of a monosulphone of dithian (isomeric with the two dioxides) has been attributed in recent years to two distinct substances: by Helfrich and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1215) to an amorphous product of the interaction of alkali sulphide and ββ′-dichlorodiethylsulphone, and by Fromm and Ungar (*Ber.*, 1923, **56**, 2286) to a substance of m. p. 200° obtained by reducing dithian trioxide (a sulphoxide sulphone). It seemed probable that the amorphous substance referred to was of high molecular weight and was related to dithian monosulphone in the same way as the "polymeric" ethylene sulphides are related to dithian (J., 1927, 1803). Confirmation of this view and of the structure of the true dithian sulphone has been obtained by repeating the experiment of Helfrich and Reid under conditions more favourable to ring closure. In this way, we obtained a crystalline monosulphone, m. p. 203°, identical with that of Fromm and Ungar. The amorphous substance of Helfrich and Reid is presumably a polyethylene polysulphide–sulphone of long open-chain structure.

The similar reaction between potassium sulphide and ββ′-dichlorodiethyl sulphoxide yielded *dithian monoxide*, ring closure taking place to the extent of 14·3% (as compared with 9·3% in the case of the sulphone; compare Cashmore and McCombie, J., 1923, **123**, 2884). The isolation of this monoxide, which we have also prepared in quantity by cautious oxidation of dithian, completes the list of possible oxidation products of dithian, namely, a monosulphoxide, a monosulphone, two stereoisomeric disulphoxides, a sulphoxide–sulphone and the disulphone.

The groups $>\overset{+}{S}\text{–}\bar{O}$, $>\overset{+}{S}\text{–}R\}\bar{X}$ and $>\overset{+}{S}\text{–}\bar{N}\cdot SO_2\cdot C_7H_7$, characteristic of sulphoxides, sulphonium salts and sulphilimines, respectively, are stereochemically analogous (Clarke, Kenyon, and

Phillips, J., 1927, 188). *cis-trans*-Isomerism is therefore to be expected in any compound in the molecule of which there are two of these groups, alike or different. In accordance with this view, we have now isolated pairs of isomeric *dithian monoxide methylsulphonium picrates* and *chloroplatinates*, $OS{<}{}^{C_2H_4}_{C_2H_4}{>}SMe\}X$, and two isomeric *dithian monoxide sulphilimines*,

$$OS{<}{}^{C_2H_4}_{C_2H_4}{>}\overset{+}{S}\cdot\overset{-}{N}\cdot SO_2\cdot C_7H_7.$$

A re-examination of the bis-sulphilimine of dithian,

$$C_7H_7\cdot SO_2\cdot\overset{-}{N}\cdot\overset{+}{S}{<}{}^{C_2H_4}_{C_2H_4}{>}\overset{+}{S}\cdot\overset{-}{N}\cdot SO_2\cdot C_7H_7$$

(Mann and Pope, J., 1922, **121**, 1052), has, moreover, shown that the substance described is a mixture, which we have separated into two crystalline isomerides.

Experimental.

Derivatives of α- and β-Dithian Dioxides.—Hydrogen chloride, passed into a solution of α-dithian dioxide in glacial acetic acid, throws down a sparingly soluble, white *monohydrochloride*, which loses hydrogen chloride on keeping (Found: Cl, 18·2. $C_4H_9O_2ClS_2$ requires Cl, 18·8%). A dihydrochloride was not detected when hydrogen chloride gas had been passed through the mixture for a further hour. β-Dithian dioxide reacts in the same way to yield a sparingly soluble *hydrochloride*.

With a solution of hydrogen bromide in glacial acetic acid, each of the dioxides yields an immediate white precipitate of a *hydrobromide*, which, however, becomes discoloured in a few minutes owing to reduction of the sulphoxide with liberation of bromine.

Addition of mercuric chloride to aqueous solutions of the α- and β-dioxides gives in each case a white, crystalline precipitate. *α-Dithian dioxide mercurichloride*, silvery plates from warm water (Found: Hg, 56·8, 57·4, 56·8. $C_4H_8O_2Cl_4S_2Hg_2$ requires Hg, 57·6%): *β-dithian dioxide mercurichloride*, which is more soluble than the preceding (Found: Hg, 56·7%).

Action of Bromine on the Dithian Dioxides.—Addition of bromine to the aqueous solutions of the α- and β-dithian dioxides yields in each case a crystalline *bromide* in orange or bright red crystals. These substances are very unstable in the air, the whole of the bromine being lost in a few minutes, the dioxide remaining behind. Determinations of the bromine content of specimens kept in an atmosphere saturated with bromine at laboratory temperature showed that even under these conditions the bromides are unstable. Parallel analyses were therefore made of the moist solid phase and

the mother-liquor, the composition of the solid being obtained by extrapolation in the usual manner. After a number of trials, the following method of analysis was adopted: to the specimen was added an excess of ammonia, and the solution allowed to evaporate to a constant weight at laboratory temperatnre in a vacuum over sulphuric acid. The bromine was determined in this mixture by Volhard's method. Subtraction of the corresponding weight of ammonium bromide from the total weight of residue gave the weight of dithian dioxide present.

The possibility that the solid migbt contain bromine in the form of hydrogen bromide (leaving free hypobromous acid in the mother-liquor) was disproved by comparative determinations of the combined bromine in the liquid by Volhard's method and of the volume of nitrogen evolved in a nitrometer on addition of ammonia.

The analyses of five pairs of samples are shown below:

	Moist solid.	Solution.	Dry solid (extrapolated).
(1)	Br, 25·1; X, 15·5	Br, 3·8; X, 7·8	Br, 68·6%
(2)	Br, 25·1; X, 10·8	Br, 6·0; X, 1·6	Br, 68·4%
(3)	Br, 24·8; X, 11·1	Br, 3·8; X, 6·2	Br, 76·6%
(4)	Br, 30·9; X, 10·3	Br, 3·5; X, 3·6	Br, 78·1%
(5)	Br, 28·0; X, 9·7	Br, 6·0; X, 7·8	Br, 76·8%

(X denotes α-dithian dioxide)

XBr_4 requires Br, 67·8%. XBr_6 requires Br, 76·0%.

Action of Potassium Sulphide on ββ'-Dichlorodiethylsulphone.—A mixture of potassium sulphide (from 14 g. of the hydroxide in a little water) with the sulphone (27 g.) in alcohol (1000 c.c.) was kept at laboratory temperature for 12 hours. The solid which had separated, consisting of potassium chloride and an amorphous substance similar to that described by Helfrich and Reid (*loc. cit.*), was removed by filtration, the solvent evaporated, and the residue crystallised from ethyl alcohol. This was identified as dithian monosulphone (2·0 g.), m. p. 203° (Found: C, 31·5; H, 5·4; *M*, cryoscopic in camphor, 163. Calc.: C, 31·5; H, 5·3%; *M*, 152). This sulphone is dimorphous, separating from glacial acetic acid in colourless needles with a straight extinction which slowly redissolve with deposition of more compact crystals. These are orthorhombic with $a:b:c = 0{\cdot}854:1:0{\cdot}696$. The following forms and mean angular values were observed with two crystals:

	m (110).	*b* (010).	*q* (011).
φ	0°0′	49°31′	49°31′
ρ	90°0′	90°0′	34°50′

The crystals were tabular with *m* large.

This sulphone is oxidised by hydrogen peroxide to the dithian trioxide, m. p. 279°, of Fromm and Ungar.

Action of Potassium Sulphide on ββ′-Dichlorodiethyl Sulphoxide.—A mixture of the sulphoxide (17·5 g.) and potassium sulphide (from 11 g. of the hydroxide) in ethyl alcohol (1000 c.c.) was kept for 12 hours at the ordinary temperature, and then evaporated. The residue was extracted with ethyl alcohol (30 c.c.) to separate the product from potassium chloride, and the extract, after evaporation, deposited crystals which, after draining on porous earthenware and recrystallisation from di-*n*-butyl ether, had m. p. 125° (yield, 0·75 g.). They were identified as *dithian monoxide*, of which a more convenient method of preparation is described below.

As the separation of this reaction product could hardly be made complete by the above method, the extent of ring closure was determined by weighing the product in the form of the more sparingly soluble dithian: the above experiment was repeated with 5·8 g. of the sulphoxide, the product reduced with an excess of zinc dust and hydrochloric acid, and the dithian removed in steam (dry weight 0·55 g.: 14·3% yield).

Oxidation of 1 : 4-*Dithian to a Monosulphoxide.*—To dithian (40 g.) dissolved in glacial acetic acid (1000 c.c.), hydrogen peroxide (5·67 g. in 500 c.c. of glacial acetic acid) was added drop by drop during 6 hours with constant stirring. After being kept for 12 hours, the mixture was distilled, the acetic acid carrying with it the unaltered dithian. The residue was evaporated several times with water to remove the remaining acetic acid. Extraction with ethyl alcohol (150 c.c.) left some dithian dioxide undissolved, and the monoxide crystallised from the solution (yield, 12·5 g.). It was recrystallised from di-*n*-butyl ether; m. p. 125° (Found: C, 35·2[illegible] H, 6·0. $C_4H_8OS_2$ requires C, 35·3; H, 5·9%). The substance [illegible] readily soluble in water and in all the common organic solvent[illegible] Crystals were obtained for goniometry by evaporation of the soluti[illegible] in water or in methyl formate. They belong to the monoclin[illegible] system, having $a : b : c = 1{\cdot}402 : 1 : 1{\cdot}878$ and $\beta = 61°20'$. T[illegible] habit is a simple combination of *m* (110) and *c* (001), with *R* ($\bar{1}$0[illegible] occasionally appearing as a small triangular face truncating [illegible] corner of the crystal. The following mean angular values w[illegible] obtained from two selected crystals:

	m (110).	*m′* (1$\bar{1}$0).	*c* (001).	*R* ($\bar{1}$01).
ϕ	0°	*101°46′	51°5′	230°55′
ρ	90°0′	90°0′	*28°40′	*44°26′

The substance yielded a *compound* with platinic chloride, a p[illegible] yellow powder (Found: Pt, 31·8. $C_8H_{16}O_2Cl_4S_4Pt$ requires [illegible] 32·0%), and a *compound* with auric chloride, a deep orange pow[illegible] (Found: Au, 45·0. $C_4H_8OCl_3S_2Au$ requires Au, 44·9%).

Isomeric Sulphonium Salts from Dithian Monoxide.—A mixture of dithian monoxide (10 g.), methyl iodide (35 g.), and ethyl alcohol (10 g.) was boiled under reflux for 8 hours and kept over-night and the sulphonium salts were then removed by filtration (17·7 g.). By crystallisation from 75% ethyl alcohol–water *α-dithian monoxide methylsulphonium iodide* was readily obtained pure (Found: I, 45·45. $C_5H_{11}OS_2I$ requires I, 45·7%). This substance is readily soluble in water and sparingly soluble in ethyl alcohol and other solvents. It separates from aqueous alcohol in feathery needles radiating from a point, or, when crystallised more slowly, in stout, monoclinic prisms. It decomposes on heating without melting. Sodium picrate in aqueous solution converts it into the corresponding *picrate*, m. p. 187° (Found: N, 11·2. $C_{11}H_{13}O_8N_3S_2$ requires N, 11·1%), which crystallises from warm water in bright yellow, monoclinic prisms or prismatic needles with an extinction angle of 36°.

The sulphonium iodide was also converted into a *chloroplatinate* (Found: Pt, 27·7. $C_{10}H_{22}O_2Cl_6S_4Pt$ requires Pt, 27·5%), crystallising in orange plates from water, in which it is sparingly soluble at the ordinary temperature.

The mother-liquors from the purification of the α-sulphonium iodide were concentrated and gave evidence of the presence of another iodide yielding a picrate of lower melting point (125—135°), but the second methiodide was not obtained pure, as it was very soluble and tended to dissociate during evaporation. A quantity (6 g.) of the crude methiodide was therefore dissolved in a little water, the equivalent of sodium picrate added, and the precipitate fractionally crystallised from hot water. In this way, the α-sulphonium picrate was quickly obtained pure (4·2 g.) and from the mother-liquor the isomeric *β-dithian monoxide methylsulphonium picrate* (1·0 g.), m. p. 137° (Found: N, 11·2%), was isolated. It is about three times as soluble in water as the α-isomeride, and crystallises in yellow, monoclinic plates or prisms with an extinction angle of 44°. A mixture of the α- and β-picrates melted at 125—170°. The picric acid was removed in ether from the acidified solution, and addition of platinic chloride and ethyl alcohol yielded the *chloroplatinate* as a pale buff precipitate soluble in water (Found: Pt, 28·0%).

Isolation of the Isomeric Sulphilimines of Dithian Monoxide.—Dithian monoxide (5 g.) and chloramine-T (18 g.) were dissolved together in the minimum quantity of cold water. The mixture, after standing for a few hours, was filtered and the precipitate fractionally crystallised from water. Two substances were found to be present in approximately equal proportions: *α-Dithian*

monoxide S-p-*toluenesulphonylimine*, m. p. 230—234° (decomp.), which crystallises from water in colourless, flat needles with a straight extinction (Found : N, 4·5. $C_{11}H_{15}O_3NS_3$ requires N, 4·6%). β-*Dithian monoxide* S-p-*toluenesulphonylimine*, m. p. 176—177° (decomp.), which is about five times as soluble as the α-compound in hot water, and crystallises best from 80% ethyl alcohol–water (Found : N, 4·7%). The crystals from water are plates having an angle of 87° and an oblique extinction. A mixture of the two isomerides melted at 167—205°.

Both α- and β-isomerides yield dithian when boiled with zinc dust and dilute acid.

Isomeric Disulphilimines of Dithian.—A mixture of dithian (5 g.) in ethyl alcohol (100 c.c.) and chloramine-T (36 g.) in water (100 c.c.) was boiled under reflux for 3 hours and cooled, and the solid products were removed by filtration. Impurities such as sodium chloride and toluenesulphonamide were removed by two extractions with boiling water (50 c.c.). The residue (4·3 g.) had the properties described by Mann and Pope (*loc. cit.*), but it was separated into two isomerides by repeated extraction with boiling *cyclo*hexanol. The α-*dithianbis*-p-*toluenesulphonylimine* was thus left behind as a white powder insoluble in *cyclo*hexanol, but readily soluble in *m*-cresol. It decomposes at 250—255° (Found : N, 6·1. $C_{18}H_{22}O_4N_2S_4$ requires N, 6·1%). This substance separates from *m*-cresol–*cyclo*hexanol in minute, elongated plates with straight extinction which are frequently twinned, showing a clearly defined re-entrant angle at each end.

The hot *cyclo*hexanol extracts of the original mixture deposited, on cooling, β-*dithianbis*-p-*toluenesulphonylimine* in tufts of leaf-shaped plates radiating from a point, which decompose at 200—210° (Found : N, 6·1%). A mixture of these two isomerides decomposed at 200—235°.

We are indebted to the Chemical Society for assistance in the purchase of materials.

THE UNIVERSITY, SHEFFIELD. [*Received, November 15th*, 1927.]

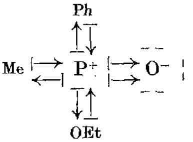
XIV.—*Some Analogous Organic Compounds of Phosphorus and Arsenic.*

By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

PHENYLMETHYLPHOSPHINIC acid reacts normally with thionyl chloride and *phenylmethylphosphinyl chloride* is easily isolated. The behaviour of this compound is that of a typical acid chloride. It

yields an *anilide* and reacts with benzoic acid, giving benzoyl *chloride*; its reaction with the carboxyl group probably explains the non-production of the *o*-carboxyphenylethylamide of phenylmethylphosphinic acid when it is allowed to react with *o*-ethylaminobenzoic acid. The acid chloride reacts very readily with water and attempts to prepare the amide and anhydride have been unsuccessful. The *methyl* and *ethyl* esters are readily obtained from the acid chloride and the corresponding alcohol. They are both colourless liquids, very readily hydrolysed, and the boiling point of each is below that of the acid chloride.

The parachor (Sugden, J., 1924, **125**, 1177; 1925, **127**, 1868 and succeeding papers) of the ethyl ester has been determined by Dr. Sugden, who finds $[P] = 420{\cdot}5$, compared with $[P] = 417{\cdot}3$ calculated for the presence of a semipolar double bond, whereas, calculated for the presence of a non-polar double bond, $[P] = 442{\cdot}1$. The constitution of the ethyl ester of phenylmethylphosphinic acid may be conveniently represented by the annexed formula.



It will be seen that the outer octet of the phosphorus atom is complete without the oxygen atom, whose octet can only be completed by sharing the two lone electrons with the phosphorus atom, leaving the latter positively and the oxygen atom negatively charged. It is clear that the methyl and ethyl esters should be capable of existing in *lævo*- and *dextro*-optically active forms, whether their constitutions are regarded from the point of view of the electronic hypothesis or because their molecules are asymmetric. In this connexion, Dr. Sugden writes, "I might mention that, in my view, this compound (the ethyl ester), unlike Phillips' sulphinic ester (*J.*, *1925*, **127**, *2552*), would be asymmetric even if the double bond were non-polar. That, however, is forbidden by the octet rule and the data for this compound give further evidence for the truth of the octet theory." * The fact that these esters are readily hydrolysed explains the reason why the preparation of the amide by the action of ammonia on the esters and of the esters by the action of the alkyl iodides on the silver salt of the acid have so far been unsuccessful. From this work, it is clear that a compound containing the $\vdots PO_2H$ grouping reacts very similarly to one containing the $-CO_2H$ grouping.

Phenylmethylarsinic acid was first prepared by Bertheim (*Ber.*,

* It is hoped to carry out experiments on the resolution of one or both of the above esters, the supply of which unfortunately is very limited (compare Pope and Gibson, J., 1912, **101**, 735, 740).

1915, **48**, 350). We have prepared it more conveniently from *phenylmethylchloroarsine* (Burrows and Turner, J., 1920, **117**, 1377; 1921, **119**, 429) by oxidation with chloramine-T (Burton and Gibson, J., 1924, **125**, 2276). It is known that this acid, unlike the corresponding phosphorus acid, is distinctly amphoteric in character. Bertheim (*loc. cit.*) showed that it can be titrated with alkali, with litmus as indicator, and he described the barium, lead and mercury salts as well as the crystalline hydrochloride and nitrate. Diphenylarsinic acid also is amphoteric and forms, for example, barium and copper salts (La Coste and Michaelis, *Ber.*, 1878, **11**, 1886; *Annalen*, 1880, **201**, 231) and also two hydrochlorides and two hydrobromides (Grignard and Rivat, *Compt. rend.*, 1919, **169**, 126); a nitrate also is referred to in the literature ("Organic Arsenical Compounds," Raiziss and Gavron, 1923, p. 366).

Attempts to prepare the ethyl ester of phenylmethylarsinic acid by the action of ethyl iodide on the silver salt have been unsuccessful. Likewise, attempts to isolate the acid chloride from the action of thionyl chloride on the acid have been unavailing and consequently it has been impossible to prepare the esters of this acid by the method used for the preparation of the analogous phosphorus compounds.

The products of the reaction of thionyl chloride on phenylmethylarsinic acid were phenyldichloroarsine and probably methyl chloride, and it is highly probable from the work which is described below that the following series of reactions takes place:

$$\begin{matrix}Ph\\Me\end{matrix}\!>\!As\!<\!\begin{matrix}O\\OH\end{matrix} \longrightarrow \begin{matrix}Ph\\Me\end{matrix}\!>\!As\!<\!\begin{matrix}O\\Cl\end{matrix} \longrightarrow \begin{matrix}Ph\\Me\end{matrix}\!>\!As\!<\!\begin{matrix}Cl_2\\Cl\end{matrix} \longrightarrow PhAsCl_2 + MeCl.$$

The same products were obtained when phenylmethylchloroarsine was substituted for the phenylmethylarsinic acid. Since, however, the methyl chloride was difficult to isolate, the reaction of thionyl chloride with diphenylchloroarsine and with diphenylarsinic acid was studied. In the case of diphenylchloroarsine, when the reaction was carried to completion, the products identified were phenyldichloroarsine, chlorobenzene and sulphur chloride. When, however, the decomposition was not carried to completion, strong evidence of the presence of diphenylarsinyl chloride was obtained, which later decomposed under the conditions of the experiment.

It is now shown that when thionyl chloride reacts with diphenylchloroarsine a definite colourless crystalline compound is formed. This has the composition $(C_6H_5)_2AsCl,SOCl_2$, and a similar compound is formed when thionyl chloride reacts with diphenylarsinic acid. When the compound $(C_6H_5)_2AsCl,SOCl_2$ is heated under the

conditions described later, it decomposes, yielding the volatile products mentioned above, and when the decomposition is carried as far as possible, the residue which remains is, in all probability, phenylarsenious oxide. The results of carrying out as nearly as possible quantitative experiments indicate that the reaction of thionyl chloride with diphenylchloroarsine may be represented by the following equations :

(1) $Ph_2AsCl + SOCl_2 \longrightarrow Ph_2AsCl,SOCl_2$.

(2) $3Ph_2AsCl,SOCl_2 \longrightarrow 2PhAsCl_2 + PhAsO + 3PhCl + SO_2 + S_2Cl_2$.

(3) $Ph_2AsCl,SOCl_2 \longrightarrow SCl_2 + {Ph \atop Ph}{>}As{<}{O \atop Cl} \longrightarrow PhCl + PhAsO$.

According to equation (2), 29·15 g. of diphenylchloroarsine should yield 9·8 g. of phenylarsenious oxide and 12·4 g. of chlorobenzene. The amounts obtained were 11·35 and 10·63 g., respectively. If decomposition is going on at the same time according to equation (3), the amount of chlorobenzene produced relative to the amount of diphenylchloroarsine will not vary, but the amount of phenylarsenious oxide will increase considerably. If the decomposition proceeded wholly according to equation (3), 29·15 g. of diphenylchloroarsine would yield 18·5 g. of phenylarsenious oxide. The results obtained, therefore, indicate that the decomposition proceeds largely according to equation (2) and that some diphenylarsinyl chloride is formed which subsequently decomposes as indicated by equation (3).

The work furnished a case of thionyl chloride acting as an oxidising agent and indicates why it is impossible, under the experimental conditions described, to obtain the acid chlorides of phenylmethylarsinic acid and diphenylarsinic acid, the possibility of the preparation of the corresponding esters through these compounds being thereby precluded.

EXPERIMENTAL.

Through the kind co-operation of Sir William Pope, the phosphenyl chloride used for this investigation was the remainder of the preparation made for the original investigations (J., 1912, **101**, 735, 740). This compound was converted into phenylmethylphosphinic acid in the manner already described (*loc. cit.*, p. 741).

Phenylmethylphosphinyl chloride, PPhMeOCl, was obtained in 94% yield by heating phenylmethylphosphinic acid (15 g.) with thionyl chloride (25 c.c.) under reflux for 30 minutes on the water-bath. The excess of thionyl chloride was removed under reduced pressure and the residue was then distilled under the same conditions. The product was obtained as a colourless liquid,

b. p. 155°/11 mm., 167°/22 mm. For analysis, the chloride was decomposed with excess of sodium hydroxide solution, and the chlorine estimated in the usual way (Found: Cl, 20·1, 20·9. C_7H_8OClP requires Cl, 20·3%).

Phenylmethylphosphinyl chloride fumes in air and has an odour reminiscent of thiocarbonyl chloride. It reacts vigorously with water and the above acid, m. p. 134°, is readily obtained. Although a dry ethereal solution of the acid chloride reacts vigorously with dry ammonia, attempts to isolate phenylmethylphosphinamide were unsuccessful.

Phenylmethylphosphinanilide was obtained by carefully adding aniline (2·5 g.) to a solution of the acid chloride (2·5 g.) in dry ether (35 c.c.), allowing the mixture to stand for 15 minutes and then adding water. The pasty solid became granular on grinding with the water. It crystallised from ethyl acetate–ligroin (b. p. 60—80°) in colourless needles, m. p. 142° (Found: N, 6·1. $C_{13}H_{14}ONP$ requires N, 6·1%).

The acid chloride (3·0 g.) reacted vigorously with the sodium salt of the acid (3·5 g., dried at 130°) and the characteristic odour of the former substance rapidly disappeared. Nothing distilled on heating to 210°/20 mm. The product was extracted with benzene, and the solvent removed under diminished pressure; the gummy residue then crystallised and was shown to be phenylmethylphosphinic acid. The anhydride, if formed under the conditions of this experiment, must be very easily hydrolysed to the acid.

When benzoic acid (3 g.) was heated with phenylmethylphosphinyl chloride (3 g.) for 10 minutes on the water-bath, and the product distilled, a liquid (2·0 g.) distilling at 200° was obtained. This was proved to be benzoyl chloride by conversion into benzamide (m. p. 124°) and benzanilide (m. p. 161°). Attempts to prepare the *o*-carboxyphenylethylamide of phenylmethylphosphinic acid were unsuccessful. When equimolecular quantities of the acid chloride and *o*-ethylaminobenzoic acid reacted under the usual conditions, a small quantity of a substance, m. p. 186°, was obtained which contained nitrogen and phosphorus. In another experiment, a substance, m. p. 168°, was isolated, but after standing in air for some time it melted at 134° (m. p. of the acid).

Ethyl phenylmethylphosphinate, PPhMeO·OEt, was prepared by warming the acid chloride (3·9 g.) together with absolute ethyl alcohol (20 c.c.) for a short time on the water-bath, removing the excess of alcohol under diminished pressure, and distilling the residue under similar conditions. The ester is a colourless, highly refractive liquid, b. p. 143°/11 mm. (Found: C, 58·3; H, 7·0; *M*, by saponification, 179·7. $C_9H_{13}O_2P$ requires C, 58·7; H, 7·1%; *M*, 184).

We are very greatly indebted to Dr. S. Sugden for carrying out the 'ollowing measurements leading to the determination of the parachor, [*P*]: $D_{4^\circ}^{20^\circ}$ 1·107, $D_{4^\circ}^{36\cdot5^\circ}$ 1·093, $D_{4^\circ}^{65^\circ}$ 1·068, whence $D_{4^\circ}^{t^\circ} = 1\cdot125 - 0\cdot00088t$.

App.	*t*.	*P*.	*D*.	*φ*.	*γ*.	Parachor.
4d	18°	5164	1·109	1·0202	40·92	420·3
4d	42	4772	1·088	1·0215	37·86	420·0
4d	62	4514	1·070	1·0223	35·84	421·2
					Mean [*P*] obsd.	420·5

($r_2 = 0\cdot139$ cm., $A = 0\cdot007767$)

P] calc.: **417·3** (for semipolar double bond), 442·1 (for non-polar louble bond).

The ester is readily hydrolysed; on boiling it for a few minutes vith 20% aqueous sodium hydroxide and cooling and acidifying the solution, phenylmethylphosphinic acid was obtained. The *methyl* ester, prepared in a similar manner to the ethyl ester, is a colourless, iighly refractive liquid, b. p. 137°/11 mm. (Found: C, 56·6; H, 6·7. $C_8H_{11}O_2P$ requires C, 56·5; H, 6·5%). Both esters have an odour ike that of the mustard oils and when heated with ammonia in ılcoholic solution do not appear to yield the amide.

Phenylmethylarsinic acid was originally prepared from phenyldichloroarsine through the arsine oxide (Bertheim, *loc. cit.*). The 'ollowing method, which avoids the use of silver salts, does not take so long and gives a better yield. Phenylmethyliodoarsine, prepared from phenyldichloroarsine (Burrows and Turner, *loc. cit.*), vas converted through the arsine oxide into phenylmethylchloroarsine (yield 80%, based on the phenyldichloroarsine). The phenylmethylchloroarsine (8·55 g.) in acetone (170 c.c.) was boiled ınder reflux with a solution of chloramine-T (23·4 g.) in water 230 c.c.) for 1 hour (see Burton and Gibson, *loc. cit.*). The acetone vas distilled off, the precipitated *p*-toluenesulphonamide removed rom the cooled aqueous solution, the filtrate evaporated to dryness, he residue extracted twice with hot alcohol, and the extracts evaporated to dryness. The residue was extracted twice with warm acetone to remove traces of *p*-toluenesulphonamide, leaving phenylmethylarsinic acid, m. p. 176—177° (yield, 96·5%). The acid may be prepared from phenylmethyliodoarsine by oxidation with chloramine-T or hydrogen peroxide, but the iodine liberated renders ts separation somewhat difficult.

In an attempt to prepare ethyl phenylmethylarsinate by means of thyl iodide (4·0 g.) and the silver salt (7·8 g.), suspended in dry ther, the product decomposed at about 90° when distilled under educed pressure.

Action of Thionyl Chloride on Phenylmethylarsinic Acid.—When

the acid (8·6 g.) and thionyl chloride (24 c.c.) were heated together on the water-bath a vigorous reaction took place, a gas (? methyl chloride) being evolved. After 30 minutes' heating, the excess of thionyl chloride was removed and the residue distilled under reduced pressure. The distillate, a colourless, highly refractive liquid, b. p. 127°/12 mm., was proved to be phenyldichloroarsine by analysis (Found: Cl, 32·6. Calc.: Cl, 32·5%) and by reduction tc arsenobenzene (m. p. 201°).

Action of Thionyl Chloride on Phenylmethylchloroarsine.—Th chloroarsine (8 g.) was treated with thionyl chloride (12 c.c.) as ir the previous experiment, heat being evolved on mixing, althougl no evolution of gas was noticed until the mixture was heated on th water-bath. After 30 minutes' heating, the thionyl chloride wa removed as before. At a higher temperature the product began t decompose. The first fraction of the distillate had the characteristi odour of sulphur chloride and gave a precipitate of sulphur o addition of water. More marked decomposition set in at a slightl higher temperature and a liquid (7·8 g.) distilled at 128°/16 mn This was proved to be phenyldichloroarsine by its giving arsen benzene on reduction. The residue in the flask (0·5 g.) was nc identified.

Action of Thionyl Chloride on Diphenylchloroarsine.—The follo ing are descriptions of typical experiments.

(*a*) When diphenylchloroarsine (m. p. 37·5°; 10·55 g.) and thion chloride were heated on the water-bath, no reaction appeared t take place until after about 10 minutes' heating. Precipitati of a distinctly crystalline, colourless substance then began and w complete in about 30 minutes. The thionyl chloride was remov as before, leaving the crystalline solid dry and uncontaminated wi tarry matter. Under diminished pressure, this melted at 188 192° (bath) and began to decompose at 195°; the distillate, b. p. 120 125°, had the characteristic odour of chlorobenzene (but a mc pungent odour also was noticed) and gave 2 : 4 : 6-trinitrochlo benzene on nitration. In another experiment, carried out und similar conditions, sulphur chloride, S_2Cl_2, was identified in t distillate.

(*b*) Diphenylchloroarsine (11·44 g.) and thionyl chloride (16 c. were treated as in (*a*), and the excess of thionyl chloride remov by heating the product at 75°/30 mm. for a short time. The dis late had no odour of sulphur chloride and no precipitate of sulp was obtained when it was mixed with water. The solid residue the flask had a characteristic odour different from that of thio chloride and weighed 16·02 g. [Calc. for $(C_6H_5)_2AsCl,SOCl_2$, 16·59 It was decomposed by heating to 200—215°/25—30 mm., deco

position not being allowed to proceed too far, and, after cooling, the product was extracted with warm aqueous ammonia; an oil remaining undissolved was removed in ether. From the aqueous solution, on acidification, diphenylarsinic acid was obtained, m. p. 171° after repeated crystallisation from dilute alcohol (Found: As, 28·5. Calc.: As, 28·6%).

(*c*) The preceding experiment was repeated with diphenylchloroarsine (29·15 g.) and thionyl chloride (42 c.c.), but after removal of the excess of the latter substance, the residue was heated at 200—215°/30 mm. until no more distillate was obtained. The final residue (11·35 g.) was shown not to contain diphenylarsinic acid. From the distillate, after extraction with dilute sodium hydroxide solution, 10·63 g. of chlorobenzene were obtained; this may have contained some small quantity of more highly chlorinated benzene derivatives. On acidification with hydrochloric acid, the sodium hydroxide solution gave phenyldichloroarsine, which yielded arsenobenzene on reduction.

Action of Thionyl Chloride on Diphenylarsinic Acid.—From diphenylarsinic acid (15 g.) and thionyl chloride (25 c.c.), by the treatment described in (*a*) above, a solid was obtained which melted at 188—192° and decomposed at about 195°/25 mm., the distillate passing over at 120—135°.* Sulphur chloride, chlorobenzene and phenyldichloroarsine were recognised in the distillate as before.

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XV.—*The Resolution of Externally Compensated* p-*Nitrobenzoylalanine.*†

By WILLIAM MORRIS COLLES and CHARLES STANLEY GIBSON.

THE resolution of those externally compensated *N*-acyl derivatives of alanine which have so far been studied in this series of investigations (Pope and Gibson, J., 1912, **101**, 939; Gibson and Simonsen, J., 1915, **107**, 798; Colles and Gibson, J., 1924, **125**, 2505) has, in

* In this and similar experiments, the boiling points of the distillates are to be regarded, not as the physical constants of the pure substances, but as the temperatures at which the various decomposition products—often superheated—passed over.

† Waser and Brauchli (*Helv. Chim. Acta*, 1924, **7**, 740) have described a convenient and sensitive test for amino-acids (except glycine and cystine): in sodium carbonate solution they give an intense dark red colour with *p*-nitrobenzoyl chloride. We have found this test more sensitive when the sodium carbonate is replaced by pyridine (compare Ingersoll and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 2930).

each case, proved fairly straightforward; but the resolution of *dl-p*-nitrobenzoylalanine has been attended with complications hardly to be anticipated with simple substances of this type.

dl-p-Nitrobenzoylalanine has a marked tendency to form partial racemates or series of mixed crystals of the diastereoisomeric salts with various alkaloids. With brucine and cinchonidine it forms partial racemates unaffected by recrystallisation. When strychnine (0·5 mol.) was used to resolve the *dl*-acid under the conditions used for the resolution of *dl*-benzoylalanine (J., 1912, **101**, 939) a mixture of the *d*A*l*B salt (colourless, soft needles) and markedly phototropic (turning deep yellow on exposure to light), long, hard needles or prisms of what approximates to the partial racemate crystallised. The *d*A*l*B salt is less soluble than the *l*A*l*B salt in water, but the above mixture had to be recrystallised four times in order to obtain the pure *d*A*l*B salt; the yield was only 39% and the acid obtained from the original mother-liquor contained only 60% of the lævo-isomeride. Although the *d*A*l*B salt was obtained pure by this method (the acid obtained from it being compared with that prepared from pure *d*-alanine), it was impossible to obtain the pure *l*A*l*B salt from aqueous solution owing to the separation of mixed crystals.

The *l*A*l*B salt is more soluble than the *d*A*l*B salt both in water and in alcohol at the ordinary temperature, but it is less soluble in alcohol at higher temperatures; the ratio of their solubilities is 1 : 1·36 at 50°. This difference in solubility led to the isolation of the pure diastereoisomeric salts, equivalent proportions of *dl*-acid and strychnine being used. The crude *l*A*l*B salt which separated at 50° was recrystallised from absolute alcohol at 50° until pure. The crude *d*A*l*B salt obtained from the original mother-liquor needed only one crystallisation from absolute alcohol at the ordinary temperature for complete purification. This resolution of *dl-p*-nitrobenzoylalanine recalls the result obtained by Ladenburg and Fischl (*Ber.*, 1907, **40**, 2279), who found that whereas the brucine hydrogen racemate separated from aqueous solution below 50°, the brucine hydrogen *l*-tartrate separated above this temperature.

The foregoing resolution of *dl-p*-nitrobenzoylalanine was extremely laborious. Frequently the salt separating consisted chiefly of the phototropic crystals referred to above (the pure diastereoisomeric salts are not phototropic). When once the pure, or nearly pure, *l*A*l*B salt had been obtained and the homogeneous solution at 50° was seeded with this, a salt reasonably rich in the *l*A*l*B constituent was deposited unless the seeding was delayed. The difficulties of the resolution are due not only to the small differences in solubility of the diastereoisomeric salts in alcohol and in water, but also to the

narked tendency to the formation of a series of mixed crystals which ire unaffected by crystallisation at the ordinary temperature and lo not markedly differ in solubility from the pure diastereoisomerides.

Externally compensated *p*-nitrobenzoylalanine is a racemic ubstance. From the melting points of mixtures of the optically ictive acids it is evident that the melting-point curve is of the ype depicted in Roozeboom's Fig. 7 (*Z. physikal. Chem.*, 1899, !8, 508).

The rotatory powers of the optically active *p*-nitrobenzoylalanines n ethyl-alcoholic solution are much lower than those of the corresponding ammonium salts in aqueous solution, but they are of the ame sign. (The rotatory powers of the optically active α-naphthaenesulphonylalanines in ethyl-alcoholic solution are of the opposite ign to those of the corresponding salts in aqueous solution : Colles nd Gibson, *loc. cit.*) The *ethyl* ester of *d*-*p*-nitrobenzoylalanine has . very much lower rotatory power, but of the same sign, in ethyllcoholic solution than the corresponding acid in the same solvent. Vhen this ester is hydrolysed with sodium hydroxide at the ordinary emperature, the rotatory power of the solution rises rapidly to a onstant value. For comparison, the *ethyl* ester of *d*-α-naphthaleneulphonylalanine was prepared : its rotatory power in ethyl-alcoholic olution, like that of the acid in the same solvent, is of the opposite ign to that of the salts of the corresponding acid in water. When he ester is hydrolysed with sodium hydroxide at the ordinary emperature the rotatory power changes slowly, finally reaching a onstant value of the opposite sign.

EXPERIMENTAL.

dl-p-*Nitrobenzoylalanine*, $CHMe(NH\cdot CO\cdot C_6H_4\cdot NO_2)\cdot CO_2H$.—l-Alanine (1 mol.; 25 g.) dissolved in *N*-potassium hydroxide l mol.; 281 c.c.) is cooled to 7°, and benzene (25 c.c.) added. -Nitrobenzoyl chloride (rather less than 1 mol.; 50 g.), dissolved 1 benzene (150 c.c.), and *N*-potassium hydroxide (1 mol.) cooled) 7° are gradually added during 75 minutes with rapid stirring. 'he temperature should not rise above 10°, neither should the otassium hydroxide be added too rapidly, otherwise a pink colortion, changing to claret-red, develops (Waser and Brauchli, *loc. it.*). The mixture is stirred for a further 15 minutes, the benzene iyer separated, and the aqueous solution acidified with concen-ated hydrochlor roduct, a microystalline mass the theoretical), ı. p. 191—193°, of *p*-nitrobenzoic id by a short ex ised from boiling ater (20 g. per g thus obtained

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(yield, 75—79%) in very pale yellow needles, m. p. 194°. The solubility of the acid per 100 g. of solvent is 0·27 in water at 26° and 19 in alcohol at 78°. It is very sparingly soluble in ether, chloroform, and benzene and moderately easily soluble in acetone. The acid is readily hydrolysed by *N*-alkalis at the water-bath temperature, deep red solutions being obtained [Found: C, 50·8, 50·8; H, 4·4, 4·1; N, 11·8; *M*, by titration with 0·1*N*-$Ba(OH)_2$, 238. $C_{10}H_{10}O_5N_2$ requires C, 50·4; H, 4·2; N, 11·8%; *M*, 238]. The *silver* salt is a white, granular substance, sparingly soluble in water (Found: Ag, 31·5. $C_{10}H_9O_5N_2Ag$ requires Ag, 31·3%).

The acid is a racemic compound, since its melting point is depressed by admixture with either of the optically active isomerides, and conversely.

Resolution of dl-p-*Nitrobenzoylalanine*.—In a preliminary experiment with strychnine and *N*-sodium hydroxide (0·5 mol. of each) and the *dl*-acid (1 mol.), an acid, m. p. 167°, [α] + 13·52° * in alcoholic solution, was obtained from the salt that separated on cooling and had been once recrystallised from water. This salt, therefore, was the *dAlB* salt.

When brucine was used instead of strychnine, a readily soluble salt separated from the deep orange solution after considerable concentration at the ordinary temperature. The salt was recrystallised from hot water, and the acid liberated from a portion in the usual way. The acid had m. p. 194° and was optically inactive. The *brucine* salt of dl-p-*nitrobenzoylalanine* crystallises in thin, yellow plates which are readily soluble in water and in alcohol and appear to contain $4H_2O$ (Found: N, 8·3; H_2O, 10·8. $C_{33}H_{36}O_9N_4,4H_2O$ requires N, 7·95; H_2O, 10·2%).

By means of cinchonidine an almost insoluble salt (10·8 g. instead of 11·2 g.) was obtained which proved also to be the partial racemate. The *cinchonidine* salt of dl-p-*nitrobenzoylalanine* was recrystallised from water and obtained in colourless, fine needles containing $3H_2O$ (Found: N, 9·5; H_2O, 7·6. $C_{29}H_{32}O_6N_4,3H_2O$ requires N, 9·6; H_2O, 7·3%). The acids obtained from the recrystallised salt and from the mother-liquor were optically inactive.

The salt obtained under similar conditions by means of cinchonine was also a partial racemate, and that obtained from quinine was an inseparable mixture of the two diastereoisomerides.

In the large-scale resolution, the *dl*-acid (100 g.; 1 mol.) and *N*-sodium hydroxide (210 c.c.; 0·5 mol.) were boiled with water (500 c.c.), strychnine (70·2 g.; 0·5 mol.) being added gradually, until complete solution was effected. The crystalline strychnine

* All rotatory powers were determined at 20° for the mercury-green (5461) line.

salt (123 g.) was filtered off after standing in the ice-chest for 16 hours. The mother-liquor (A) was worked up later.

The salt obtained was a mixture, a part of which was phototropic, turning deep yellow on exposure to daylight. The salt was recrystallised from 700 c.c. of boiling water and 111·4 g. crystallised. This in alcoholic solution had [α] − 11·19° (c = 1·4092). The rotatory power gradually diminished on recrystallisation and became constant after four recrystallisations under similar conditions. This constant value was confirmed after a fifth crystallisation; the rotatory power of the salt which crystallised was then identical with that of the salt obtained from the mother-liquor. Further crystallisation from absolute alcohol caused no alteration in the rotatory power. 47·7 G. of the pure strychnine salt of the *d*-acid were obtained.

The *strychnine* salt of d-p-*nitrobenzoylalanine*,

$$CHMe(NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2){\cdot}CO_2H,C_{21}H_{22}O_2N_2,1\tfrac{1}{2}H_2O,$$

crystallises from hot water (solubility at 20°, 0·4; at 100°, 4) in *colourless needles which are not phototropic (Found:* H_2O, 4·1. Required for $1\frac{1}{2}$ H_2O : H_2O, 4·5%. Found in anhydrous material: N, 9·9. $C_{31}H_{32}O_7N_4$ requires N, 9·8%). Its rotatory power in ethyl alcohol was [α] − 1·90° (*c* = 1·5018, *l* = 4, α = − 0·114°). Other values obtained under similar conditions were [α] − 2·00° and − 1·83°. That the salt was pure was proved by the rotatory power of the acid obtained from it (see below). A solution of the anhydrous salt in absolute alcohol slowly deposits large, colourless prisms and the solubility of the salt in alcohol diminishes from 3·7 to 0·54 at the ordinary temperature. The prisms, kept in a vacuum desiccator or exposed to air, rapidly effloresce.

The acid liberated from the mother-liquor (A) in the usual way was recrystallised from 2400 c.c. of water. It then weighed 44·1 g. and had m. p. 189—190° (softening at 168°). In aqueous solution as the ammonium salt, it had [α] − 10·35° (*c* = 2·028, *l* = 4). It contained *only* 60% *of the l-acid.*

The mother-liquors from the first four crystallisations of the above strychnine salt were concentrated in two portions, and the strychnine salts separating on cooling collected. After repeated recrystallisation from boiling water, decolorisation with charcoal, and recrystallisation from absolute alcohol, 9·2 and 13·3 g., respectively, of samples of strychnine salt of identical and definitely constant rotatory power were obtained; [α] − 40·16°, − 40·71°, − 40·42° (*c* = 0·9130, 0·9828, 1·0222; *l* = 4 in ethyl alcohol). Although at the time it was believed that this was pure strychnine *l*-acid salt, subsequent work showed that it still contained *dAlB* salt.

In view of the difficulties indicated above, an approximate deter-

mination of the solubilities of the two diastereoisomeric salts in absolute alcohol was made. The *lAlB* salt was the less soluble in warm alcohol. At 50°, the solubilities in alcohol were: 2·68 for the *lAlB* and 3·64 for the *dAlB* salt. This difference in solubility, although small, indicated a method for the isolation of the pure salts.

The following conditions are typical of a series of experiments: To a solution of the *dl*-acid (10 g.; 1 mol.) in boiling alcohol (200 c.c.), strychnine (14·04 g.; 1 mol.) was added gradually. When the alkaloid had dissolved, the solution was placed in a thermostat at 50° and seeded with the purest strychnine *l*-acid salt available. A nodular deposit of radiating tufts of needles formed rapidly and the deposition was complete in 5 hours. The mother-liquor (B) was poured off and the deposit was washed with warm absolute alcohol and dried as rapidly as possible by suction (yield, 10—12 g.). The rotatory power in ethyl alcohol was $[\alpha] - 36{\cdot}2°$ ($c = 0{\cdot}7916$, $l = 4$). The mother-liquor (B) was treated as described later.

The purification of the above crude strychnine *l*-acid salt was very difficult. Successive fractional crystallisations from absolute alcohol at 50° was the only effective method; recrystallisation from water or from alcohol at the ordinary temperature was useless. The method was naturally wasteful of material. The acid liberated from a salt which had reached a rotatory power of $[\alpha] - 45{\cdot}0°$ had $[\alpha] - 47{\cdot}8°$ (as ammonium salt in water; $c = 1{\cdot}5040$, $l = 4$) and contained 96·5% of the *l*-acid. A specimen of a salt which had a rotatory power of $[\alpha] - 46{\cdot}6°$ gave an acid having $[\alpha] - 48{\cdot}35°$ under similar conditions and containing 97·0% of *l*-acid. Finally, 42·5 g. of strychnine *l*-acid salt having $[\alpha] - 40{\cdot}0°$, after four fractional crystallisations at 50° from absolute alcohol, gave 9·0 g. of pure strychnine *l*-acid salt having a rotatory power identical with that of the salt remaining in the mother-liquor.

The *strychnine* salt of l-p-*nitrobenzoylalanine*,

$$CHMe(NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2){\cdot}CO_2H,C_{21}H_{22}O_2N_2,C_2H_5{\cdot}OH,$$

crystallises from absolute alcohol in colourless needles which are not phototropic (Found: $C_2H_5{\cdot}OH$, 7·15. $C_{31}H_{32}O_7N_4,C_2H_5{\cdot}OH$ requires $C_2H_5{\cdot}OH$, 7·3%. Found in "anhydrous" substance: N, 9·95. $C_{31}H_{32}O_7N_4$ requires N, 9·8%). The "anhydrous" material in ethyl alcohol at 20° gave $\alpha - 1{\cdot}433°$ ($c = 0{\cdot}7340$, $l = 4$); whence $[\alpha] - 48{\cdot}8°$.

The resolution described above was frequently complicated by the separation, along with the nodular deposit, of large prisms (partial racemate) which were strongly phototropic. This invariably occurred when the solution was not seeded at once. When it did

occur, the salt was redissolved and the experiment repeated. This explanation was proved correct by the following experiments: (a) 10 G. of the *dl*-acid were treated exactly as described above and the solution in the thermostat at 50° was seeded with the above-mentioned phototropic partial racemate. The crystalline deposit consisted of needles and prisms (no nodules), formed during 5 hours. The markedly phototropic crystals were separated as previously described. The rotatory power in ethyl alcohol ($c = 0{\cdot}8570$, $l = 4$) was $[\alpha] - 26{\cdot}6°$. (b) 10 G. of the *dl*-acid were treated with the equivalent quantity of strychnine in double the quantity of alcohol and the solution was allowed to cool to the ordinary temperature. After 8 hours, 76% of the salt had crystallised and consisted of small, well-formed, phototropic, efflorescing prisms and needles. The rotatory power in ethyl alcohol ($c = 1{\cdot}2438$, $l = 4$) was $[\alpha] - 24{\cdot}06°$. The deposit obtained from the mother-liquor on standing had $[\alpha] - 21{\cdot}8°$ under the same conditions.

From the mother-liquor (B), allowed to cool to the ordinary temperature, a crystalline mixture of phototropic needles and non-phototropic, efflorescing prisms was deposited (8—10 g.). The rotatory power of an average specimen of this mixture was $[\alpha] - 15°$ (in alcohol). This salt therefore contained the greater proportion of the *dAlB* salt. Under the conditions of the first resolution, this would have required five successive recrystallisations from water for complete purification. The solubilities of the *dAlB* and the *lAlB* salt in alcohol at 20° being 0·69 and 0·91, respectively, this difference was used to obtain pure *dAlB* salt from the mixture. The mixture was dissolved in sufficient boiling absolute alcohol to make a 1·5% solution, and this was seeded with pure *dAlB* salt and kept for at least 24 hours. The crystalline deposit (45—50% yield) had an average rotatory power of $[\alpha] - 3°$ (in alcohol). One recrystallisation of this from boiling water was sufficient for complete purification. The mother-liquor was concentrated, and the crystalline salt which separated (30—35%) had an average rotatory power of $[\alpha] - 40°$ (in alcohol) and therefore contained an excess of the *lAlB* salt.

Optically Active p-*Nitrobenzoylalanines*.—d-p-*Nitrobenzoylalanine* was isolated from the pure strychnine *d*-acid salt by grinding it with a slight excess of dilute aqueous ammonia, filtering off the strychnine, and acidifying the filtrate, after thorough extraction with chloroform, with an excess of hydrochloric acid. The acid was recrystallised from boiling water (10 g. in 110 c.c.) and obtained in long, very pale yellow needles, m. p. 168·5—169° (Found: C, 50·8; H, 4·2; N, 11·8. $C_{10}H_{10}O_5N_2$ requires C, 50·4; H, 4·2; N, 11·8%).

The rotatory power was (as ammonium salt) [α] + 51·40° in water (c = 1·7940, l = 4, α = + 3·688°) and [α] + 15·76° in ethyl alcohol (c = 1·9882, l = 4, α = + 1·254°).

The optical purity of this compound was proved by comparison with that of the p-nitrobenzoyl derivative of pure d-alanine (kindly supplied by Sir William Pope, F.R.S.) prepared by the method already described. This preparation (as ammonium salt) had [α] + 51·32° in water (c = 1·5964, l = 4, α = + 3·277°). The m. p. was 168·7—169° and was not affected by admixture with the above compound.

d-p-Nitrobenzoylalanine has a solubility in water at 15° of 0·26 and is easily soluble in alcohol. A mixture with a small quantity of pure dl-acid had m. p. 162—167°, and with a larger quantity 191·5°. A specimen having [α] + 15·15° (as ammonium salt in water) and therefore containing 64·7% of the pure d-acid softened at 165° and melted at 188·5—189·5°. Another specimen having [α] + 45·82° (as ammonium salt in water) and containing 94·6% of the pure d-acid had m. p. 167°.

l-p-*Nitrobenzoylalanine* was obtained in the same manner from the pure strychnine l-acid salt. It crystallised from water in long, pale yellow needles, m. p. 167·5—168° (Found: M, by titration, 238·1. $C_{10}H_{10}O_5N_2$ requires M, 238). As ammonium salt, it had [α] − 51·66° in water (c = 1·6462, l = 4, α = − 3·402°) and [α] − 15·81° in ethyl alcohol (c = 0·9960, l = 4, α = − 0·628°). A specimen of acid having [α] − 47·8° (as ammonium salt in water) and containing 96·5% of l-acid had m. p. 165·5—166·5°. Another specimen having [α] − 48·35° (as ammonium salt in water) and containing 97·03% of l-acid had m. p. 166—167°. A third specimen having [α] − 44·99° (as ammonium salt in water) and containing 93·7% of l-acid had m. p. 162·5—163·5° (? eutectic point).

Owing to the difficulty of obtaining the pure strychnine l-acid salt, attempts were made to purify the optically impure acid by various methods. On recrystallisation from water, the l-acid content only changed from 79·5% to 78·7%. Although the solubility of the optically active acid in alcohol is markedly greater than that of the racemic compound, recrystallisation from alcohol was not completely successful. 10·75 G. of a specimen of the acid containing 78·7% of the l-acid, dissolved in 50 c.c. of boiling alcohol, yielded after 48 hours 6 g. of prismatic needles which contained 69·7% of l-acid. The residue recovered from the mother-liquor, after recrystallisation from water, weighed 2·75 g. and contained 93·7% of l-acid (? eutectic).

The method of purifying optically impure l-α-naphthalenesulph-

onylalanine (Colles and Gibson, *loc. cit.*) was tried, cinchonidine being used (see above). 10 G. of acid containing 60% of *l*-acid were dissolved in water, and sufficient cinchonidine to combine with the racemic acid present and sufficient standard sodium hydroxide to combine with the excess of *l*-acid were added. The whole was brought into solution on boiling and the crystalline salt separated on cooling. The acid recovered from the filtrate was optically inactive, showing that the cinchonidine *l*-acid salt has the same solubility as the partial racemate (see above). A similar experiment was attempted, sufficient strychnine being used to combine with the *d*-acid salt, which is the less soluble in water. The acid recovered from the mother-liquor contained 77% of *l*-acid, whereas the acid used contained 60%.

The *ethyl* ester of dl-p-*nitrobenzoylalanine*,

$$CHMe(NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2){\cdot}CO_2Et,$$

is easily prepared by the alcohol–hydrogen chloride method in 75% yield, and crystallises from benzene–ligroin in waxy needles, m. p. 117·5—118°. It is readily soluble in alcohol and chloroform and sparingly soluble in ether (Found: N, 10·6. $C_{12}H_{14}O_5N_2$ requires N, 10·5%). The amide is not obtained by passing dry ammonia into a benzene–ether solution of the ester.

The *ethyl* ester of d-p-*nitrobenzoylalanine* is prepared from *d*-*p*-nitrobenzoylalanine by the same method in 77% yield. By recrystallising from the same mixture of solvents it is obtained in colourless needles, m. p. 121—121·5°, which retain benzene very obstinately. Its solubility is rather greater than that of the externally compensated ester (Found: N, 10·5%). Its rotatory power in ethyl alcohol was very small; $c = 1{\cdot}416$, $l = 4$, $\alpha = 0{\cdot}075°$, whence $[\alpha] + 1{\cdot}32°$.

1·1328 G. of the ester were dissolved in 90% ethyl alcohol, rather more than the calculated quantity of *N*/2-sodium hydroxide was added, and the whole made up to 100 c.c. The rotatory power was observed immediately after mixing in a 4-dcm. tube and showed that hydrolysis had commenced; $\alpha = +1{\cdot}45°$ (the corresponding value for the unchanged ester in alcoholic solution would have been $+0{\cdot}06°$) and after 10 minutes, $\alpha = +2{\cdot}07°$. After 2½ hours a constant value of $\alpha = +2{\cdot}43°$ was observed. The *d*-acid recovered from the solution and after recrystallisation had m. p. 168·5°, alone or mixed with pure *d*-*p*-nitrobenzoylalanine.

An attempt was made to purify an optically impure specimen of *l*-*p*-nitrobenzoylalanine (containing 64·7% of the pure *d*-acid) by converting it into its ethyl ester. The optically active ester, being the more soluble, remained in the mother-liquor together with any

*impurities on recrystallisation. The low rotatory power rendered criteria of purity almost impossible.**

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XVI.—*The Stereochemistry of Reduced Quinoxalines. Part III. The Resolution of Externally Compensated* α- *and* β-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalines.*

By CHARLES STANLEY GIBSON, JOHN HENRY NUTLAND, and JOHN LIONEL SIMONSEN.

2 : 3 : 7-TRIMETHYLQUINOXALINE (von Pechmann, *Ber.*, 1888, **21**, 1414) is easily reduced by sodium and ethyl alcohol to a mixture of the two stereoisomeric derivatives, $C_6H_3Me<\genfrac{}{}{0pt}{}{NH\cdot CHMe}{NH\cdot CHMe}$, which are conveniently separated by the method described in the present paper. The α-, or lower-melting, compound constitutes about 30% of the mixture.

Both these compounds are externally compensated bases and the

* For comparison with the above results the *ethyl* esters of dl- and d-α-*naphthalenesulphonylalanine* (Colles and Gibson, *loc. cit.*) were studied.

dl-α-Naphthalenesulphonylalanine was converted in the usual manner into its *ethyl* ester, which was obtained in 75% yield. Recrystallised from ethyl alcohol, it was obtained in hard rhombs, m. p. 104° (Found: C, 58·6; H, 5·4. $C_{15}H_{17}O_4NS$ requires C, 58·6; H, 5·5%). The amide was not obtained by the method described above.

d-α-Naphthalenesulphonylalanine was similarly converted into its *ethyl* ester, which crystallised from benzene–ligroin in colourless needles, m. p. 83·5—84° (Found: N, 4·6%). In ethyl alcohol it had [α] − 47·15° (*c* = 1·9842, *l* = 4, α = − 3·74°).

1·1186 G. of the ester were dissolved in 50 c.c. of ethyl alcohol, mixed with rather more than the calculated quantity of *N*/2-sodium hydroxide, and made up to 100 c.c. The rotatory power, α = − 0·87°, observed immediately after mixing showed that hydrolysis had barely commenced. After 22½ hours, the rotatory power was α = − 0·11° and after 67 hours a constant rotatory power of α = + 0·21° was observed. The acid recovered from the solution was recrystallised and had m. p. 140·5—141·5°, alone or mixed with pure *d*-α-naphthalenesulphonylalanine.

α-base is readily resolved into its optically active components by means of *d*- and *l*-tartaric acids under similar conditions to those adopted for the resolution of externally compensated 2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline (Gibson, J., 1927, 342). The melting points of the pure optically active α-bases being 61·5—62·5° and mixtures of the optically active bases having melting points below 60°, whereas the melting point of the externally compensated base is 71°, it follows that the last is a racemic compound. The *d*- and *l*-α-bases have distinctly higher rotatory powers than those of the optically active 2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalines (Gibson, *loc. cit.*).

The following is a summary of the constants of *racemic* α-2 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline, of its optically active components and of those derivatives which are described in the present paper :

	M. p.	$[M]^{20°}_{5461}$.
rac-α-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*	71°	—
dl-α-1 : 4-*Diacetyl*-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*	147	—
d-α-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*	61·5—62·5	+206·9°
l-α-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*	61·5—62·5	−206·9
d-α-1 : 4-*Di*-m-*nitrobenzoyl*-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*	—	−466·4
l-α-1 : 4-*Diacetyl*-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*	164·5—165·5	+427·2

The externally compensated β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* forms the greater part of the reduction product of 2 : 3 : 7-trimethylquinoxaline, and being the less soluble, is the more easily isolated. No crystalline salt of this base was obtained with *d*-camphor-10-sulphonic acid, *d*-α-bromocamphor-π-sulphonic acid or *d*-tartaric acid. When the base was condensed with *d*-oxymethylenecamphor (Pope and Read, J., 1913, **103**, 1516; Gibson and Simonsen, J., 1915, **107**, 1157) a crystalline mixture was obtained. From this, the less soluble d-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-d-*methylenecamphor* (the 1 : 4-di-*d*-methylenecamphor derivative was not obtained) was obtained pure by repeated crystallisation from ethyl alcohol. It is probable that the diastereoisomeride, *l*-β-2 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalino-1-*d*-methylenecamphor, was not obtained optically pure. Pure l-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-l-*methylenecamphor* was, however, prepared both from the externally compensated base and from the base obtained by hydrolysis of the more soluble fractions from the first resolution (see below).

These compounds are highly crystalline and have very high

rotatory powers, $[\alpha]_{5461}^{20^\circ} = \pm 1309^\circ$. Being derivatives of secondary bases, the difficulty with which they are hydrolysed probably accounts for the fact that they show no mutarotation even in the presence of acetic acid during 24 hours at the ordinary temperature. Pope and Read (*J.*, *1912*, **101**, 2387) have shown that there are two methods for effecting the hydrolysis of oxymethylenecamphor derivatives of primary and of secondary amines: (1) by titrating an alcoholic solution of the condensation product with bromine, and (2) in the case of the condensation product of secondary amines when the nitrogen is in a closed ring, by hydrolysis with hydrochloric acid (Pope and Read, *J.*, 1913, **103**, 1580). Titration of an alcoholic solution of the condensation product with bromine was found to be unsatisfactory, since the reaction did not proceed normally, and consequently the hydrolysis of the two stereoisomeric condensation products with hydrochloric acid was carefully investigated.

The hydrolysis is conveniently effected by passing steam into a suspension of the condensation product in concentrated hydrochloric acid until oxymethylenecamphor ceases to distil. Under the most favourable conditions, *i.e.*, carrying out the steam distillation in the minimum time—usually 15 minutes—and superheating being avoided, the hydrolysis is attended with the formation of some small quantity of resinous and other by-products, but the base is easily separated in the usual way.

After purification, the base obtained from either condensation product showed but feeble optical activity and the experimental work indicates that very considerable racemisation of the base had occurred during the hydrolysis. For example, a part of the expected *d*-β-base, having a small optical activity, was converted into its diacetyl derivative and this was found to be a mixture. On recrystallisation from water, the aqueous filtrate had a marked dextrorotatory power. Another portion was converted into its oxalate in acetone solution; the base recovered from the less soluble oxalate had a small dextrorotatory power, whereas that obtained from the more soluble portion of the oxalate had a larger dextrorotatory power. Similarly, the expected *l*-β-base had only a small lævorotatory power. The corresponding diacetyl derivative yielded on crystallisation a specimen which was optically inactive and the mother-liquor from this showed a considerable lævorotation. The oxalate of the same specimen of base which separated from acetone solution gave optically inactive base, and the base recovered from the oxalate remaining in solution was definitely lævorotatory.

The hydrolysis of oxymethylenecamphor derivatives of this type by means of concentrated hydrochloric acid has not been extensively

studied and it appears that this is the first time it has been shown that the hydrolysis of such compounds may be attended with racemisation, even when the asymmetric centres in the compounds are not affected chemically during the reaction. If the hydrolysis by means of concentrated hydrochloric acid could be brought about at the ordinary temperature, as in the case of the dimethylpiperazino-*d*-methylenecamphors (Pope and Read, J., 1912, **101**, 2337), it is possible that racemisation of the base might not take place. The present work provides evidence that the hydrolysis of the diacetyl derivatives of the active bases is also attended with racemisation of the base.

Although the pure *d*- and *l*-β-bases have not been obtained, it is possible to conclude that the externally compensated β-base is a racemic compound. The inactive base has m. p. 97—98° and mixtures of the active bases have been obtained with melting points lower and higher than this value.

Experimental.

dl-α- *and* β-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalines*.—The 2 : 3 : 7-trimethylquinoxaline (von Pechmann, *loc. cit.*) was purified by steam distillation and isolated from the distillate, saturated with ammonium sulphate, by extraction with benzene.

The reduction was carried out exactly as described in Part II (Gibson, *loc. cit.*). In the earlier experiments an attempt was made to separate the two tetrahydro-bases formed by means of oxalic acid and it was thus found possible to separate the higher-melting β-base in a state of purity, but the lower-melting α-base could not be obtained pure when the mother-liquors were worked up. The most convenient method for obtaining the two bases was as follows: The solid mixture (20 g.) was extracted in a Soxhlet apparatus with ligroin (b. p. 40—60°; 200 c.c.), and the cooled solution kept for some hours; a slightly yellowish base (9 g.) then crystallised. This consisted of the nearly pure β-*base*. It was purified by crystallisation from ligroin (b. p. 60—80°) until its melting point was unaltered and was thus obtained in colourless, flat plates, m. p. 97—98° (Found: C, 75·3; H, 8·9. $C_{11}H_{16}N_2$ requires C, 75·0; H, 9·1%). The oxalate crystallised from acetone, in which it was only sparingly soluble, in colourless nodules, m. p. 138—140°, decomp. 152—154°.

dl-β-1 : 4-*Diacetyl*-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was prepared by heating the base with an excess of acetic anhydride for 1 hour on the water-bath. It crystallises from ligroin or water in colourless, glistening prisms, m. p. 131° (Found: C, 69·1; H, 7·5. $C_{15}H_{20}O_2N_2$ requires C, 69·2; H, 7·7%).

The ligroin filtrate from which the β-base had been removed was evaporated to dryness, the residue dissolved in alcohol (40 c.c.), and concentrated hydrochloric acid (20 c.c.) added. After some hours, the greater part of the β-base remaining in the mixture crystallised as the sparingly soluble hydrochloride. The filtrate was evaporated to dryness, the residue suspended in water, and ammonia added in slight excess. The liberated base was distilled in steam and isolated from the distillate by extraction with benzene. This dl-*α-base* crystallised from ligroin (b. p. 40—60°) in almost colourless prisms, m. p. 71°. The yield of the α-base was approximately 30% of the total reduction product (Found: C, 75·0; H, 8·7. $C_{11}H_{16}N_2$ requires C, 75·0; H, 9·1%).

dl-α-1 : 4-*Diacetyl*-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, prepared from the base and acetic anhydride, crystallised from water in colourless prisms, m. p. 147° (Found: C, 69·1; H, 7·7. $C_{15}H_{20}O_2N_2$ requires C, 69·2; H, 7·7%).

Resolution of dl-*α*-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*.—To a boiling solution of *d*-tartaric acid (24 g.) in water (180 c.c.) the *dl*-α-base (24·6 g.) was added gradually, the liquid was boiled until a clear solution was obtained and was then cooled, and after 3 hours the crystals were separated and washed with a little water. The salt thus obtained (24·2 g.) was the crude *d*-tartrate of the *d*-α-base. The filtrate and washings were used for the separation of the *l*-α-base.

The above crude tartrate was decomposed with a slight excess of ammonia, the base was isolated and again converted into the *d*-tartrate under the same conditions as above, and the salt was separated and again treated in the same way; pure d-α-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* d-*tartrate* was then obtained. It crystallised from water in colourless needles containing $2H_2O$ (Found: N, 7·9; H_2O, 9·9. $C_{15}H_{22}O_6N_2,2H_2O$ requires N, 7·7; H_2O, 9·9%).

From the original mother-liquor and the washings from the first separation of the crude *d*-α-base *d*-tartrate, the base (12 g.) was liberated and dissolved in boiling water containing *l*-tartaric acid (11 g.). The salt (20 g.) which crystallised on cooling was reconverted into the free base (8·8 g.) and this was again combined with *l*-tartaric acid (8·1 g.) under the same conditions; the pure salt then crystallised from the solution on cooling.

l-α-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* l-*tartrate* crystallised from water in colourless needles containing $2H_2O$ (Found: N, 7·9. $C_{15}H_{22}O_6N_2,2H_2O$ requires N, 7·7%).

The *d*-α-base *d*-tartrate had α + 1·96° (*c* = 0·9592), whence

$[\alpha] = + 51{\cdot}1°$,* and the *l*-α-base *l*-tartrate had α − 1·77° (*c* = 0·8576), whence [α] = − 51·6°.

The pure d- and l-α-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalines* were each obtained from the corresponding tartrate by treatment in aqueous suspension with a slight excess of ammonia; the base was extracted with benzene and after removal of the solvent the residue was extracted in a Soxhlet apparatus with ligroin (b. p. 40—60°). The bases crystallised in very faintly yellow prisms, m. p. 61·5—62·5° in each case [Found: (for *d*-base) N, 15·9; (for *l*-base) N, 15·7. $C_{11}H_{16}N_2$ requires N, 15·9%]. Some mixtures of the two bases had melting points lower than 60°. The *d*-α-base had α + 4·29° (*c* = 0·9120), whence [α] = + 117·5°, and the *l*-α-base had α − 4·29° (*c* = 0·9124), whence [α] = − 117·5°.

d-α-1 : 4-*Di*-m-*nitrobenzoyl*-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was prepared by heating the *d*-α-base with rather more than the theoretical quantity of *m*-nitrobenzoyl chloride in pyridine solution on the water-bath. The product was crystallised three times from ethyl alcohol and obtained as a microcrystalline, pale yellow powder. It gradually decomposed on heating without melting (Found: N, 12·1. $C_{25}H_{22}O_6N_4$ requires N, 11·8%). It gave α − 0·91° (*c* = 0·2312), whence [α] = − 98·4°.

l-α-1 : 4-*Diacetyl*-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, prepared from the *l*-α-base in the usual way, crystallised from water in colourless, flat prisms which contained water of crystallisation. It was obtained anhydrous by drying in a desiccator over sulphuric acid and then melted at 164·5—165·5° (Found: N, 11·3. $C_{15}H_{20}O_2N_2$ requires N, 10·8%). It had α = + 5·69° (*c* = 0·8656), whence [α] = + 164·3°.

Resolution of dl-β-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*.—Attention has already been directed to the difficulties encountered in effecting the resolution of this base. The salts with the optically active acids already mentioned were uncrystallisable gums. The *dl*-β-base (83 g.) was dissolved in acetic acid (50%, 400 c.c.) and *d*-oxymethylenecamphor (85 g.) in alcohol (400 c.c.) was added. The mixture was heated on the water-bath for 15 minutes and on cooling a crystalline solid (133 g.) separated. The condensation product remaining in solution was precipitated by the addition of dilute sodium hydroxide solution.

The less soluble fraction was repeatedly crystallised from ethyl alcohol until its melting point was constant and in this way pure

* The rotations of the active compounds described in this paper were determined in ethyl-alcoholic solution at 20° in a 4-dcm. tube for the mercury-green (5461) line (except where stated otherwise).

d-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-d-*methylen*
camphor, $\underset{NH\cdot CHMe\cdot CHMe}{C_6H_3Me}$—$\underset{}{N\cdot CH{:}C}$—$\underset{CO}{C_8H_{14}}$, was obtained in well-forme
yellow prisms, m. p. 243—244° (Found: C, 78·4; H, 8·7. $C_{22}H_{30}ON$
requires C, 78·1; H, 8·9%). It had α_{5461} + 26·77° and α_{5780} +
21·30° (c = 0·5100), whence $[\alpha]_{5461}$ = + 1312° and $[\alpha]_{5780}$ = +
1044°. When acetic acid was added to the alcoholic solution n
mutarotation was observed during 24 hours at the ordinary ten
perature.

By working up the earlier mother-liquors from the recrysta
lisation of the condensation product and also the product pr
ecipitated by dilute sodium hydroxide a more soluble fraction wa
obtained which, after several crystallisations from dilute alcoh
and then from ligroin–benzene, softened at 110° and melted a
170—175° (Found: N, 7·9. $C_{22}H_{30}ON_2$ requires N, 8·3%). Fro
its behaviour on heating it was believed that it was the optical
impure diastereoisomeric condensation product. The analysis wa
somewhat difficult to carry out owing to the substance bein
hygroscopic. It had α_{5461} + 16·54° and α_{5780} + 13·65° (c = 0·890(
whence $[\alpha]_{5461}$ = + 448° and $[\alpha]_{5780}$ = + 383°.

As the more soluble fraction could not be purified, the cru
substance (45 g.) recovered from the solution was heated to boilin
with concentrated hydrochloric acid (500 c.c.) and steam passe
through the solution until *d*-oxymethylenecamphor ceased to dis
(15 minutes). The yellow solution which remained contained son
resinous material which was easily separated. The solution w
cooled, extracted with benzene to remove neutral products, an
then treated with a slight excess of aqueous ammonia. The sen
solid which separated was extracted with benzene, and the latt
solution, after being washed, dried with potassium hydroxide. T
benzene solution after filtration from a further small quantity
resinous material was evaporated to dryness, and the base th
obtained purified by extraction with ligroin * (b. p. 40—60°
yield 15·4 g. This base had m. p. 96—99° and had a small læv
rotatory power, α − 0·16° (c = 0·9596), whence [α] = − 4·17°.

l-β-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-l-*methy*
enecamphor † was prepared from the feebly lævorotatory ba
referred to above and *l*-oxymethylenecamphor, the condensati
and purification of the less soluble product being carried out exact
as for the stereoisomeric substance. After repeated crystallisati

* In later experiments it was found more convenient to purify the base
steam distillation.

† The same compound was obtained when the pure *dl*-β-base was condens
with *l*-oxymethylenecamphor.

from ethyl alcohol, the pure substance, m. p. 243—244°, was obtained in yellow prisms (Found: N, 8·35. $C_{22}H_{30}ON_2$ requires N, 8·3%) and its properties corresponded exactly with those of the stereoisomeride. It had α_{5461} — 25·63° and α_{5780} — 20·50° (c = 0·4902), whence $[\alpha]_{5461}$ = — 1307° and $[\alpha]_{5780}$ = — 1045°.

Hydrolysis of d-β-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-d-*methylenecamphor and of its Stereoisomeride*.—The hydrolysis of these substances was carried out under the conditions previously described, the base in each case being isolated by steam distillation.

The base separated from the *d*-oxymethylenecamphor derivative crystallised from ligroin in glistening, colourless, thin plates, m. p. 106—107·5°, and the melting point after admixture with the *dl*-β-base was depressed to 90—95° (Found: N, 15·6. $C_{11}H_{16}N_2$ requires N, 15·9%). This base in ethyl-alcoholic solution was only feebly dextrorotatory. The diacetyl derivative crystallised slowly from water in colourless prisms, and later, when the solution was stirred, needles separated, indicating that the diacetyl derivative was a mixture. This was confirmed by the melting point, since the substance softened at 108—109° and did not become clear until 123—124°. The aqueous filtrate was dextrorotatory, giving in a 4-dcm. tube at 20° α_{5461} = + 2·7°. When a concentrated acetone solution of the base was mixed with the calculated quantity of oxalic acid, also in acetone solution, and kept in the ice-chest, the oxalate crystallised slowly in rosettes of glistening needles differing in appearance from the oxalate of the *dl*-β-base. The needles softened at 138° and decomposed at 144°. The base which was obtained from the oxalate had m. p. 105—106° after crystallisation from ligroin, and showed a small but definite dextrorotation in ethyl-alcoholic solution at 20°: c = 2·2490, l = 4, α_{5461} = + 0·23°, whence $[\alpha]_{5461}$ = + 2·56°. From the oxalate of the base remaining in the mother-liquor, the recovered base, after recrystallisation from ligroin, had m. p. 105—107°, softening at 102°. It had α + 0·05° (c = 0·6096, l = 2), whence $[\alpha]$ = + 4·1°.

The base separated from the hydrolysis of the *l*-oxymethylenecamphor derivative was purified by distillation in steam and crystallisation from ligroin. It was obtained in glistening, thin plates, m. p. 105—106°, and when mixed with the *dl*-β-base it softened at 90° and melted at 94—95° (Found: N, 16·0. $C_{11}H_{16}N_2$ requires N, 15·9%). Its lævorotation in ethyl-alcoholic solution was very small. The diacetyl derivative, after crystallisation from ligroin and then from water, separated in hard, glistening prisms, m. p. 132—132·5°, and this was not depressed on admixture with the diacetyl derivative of the *dl*-β-base. It was optically inactive in ethyl-alcoholic solution. The aqueous filtrate was lævorotatory,

giving in a 4-dcm. tube at 20° $\alpha_{5461} = -1{\cdot}0°$. On hydrolysis of the acetyl derivative present in this aqueous solution with hydrochloric acid, complete racemisation took place, the base liberated being optically inactive in ethyl-alcoholic solution. The oxalate prepared in acetone solution, was deposited slowly in hard nodules. The base obtained from this crystalline oxalate, after crystallisation from ligroin, had m. p. 95—99° and was optically inactive in ethyl-alcoholic solution. The base recovered from the oxalate remaining in the acetone solution had, after crystallisation from ligroin, m. p. 105—108°. It had $\alpha - 0{\cdot}09°$ ($c = 1{\cdot}2492$), whence $[\alpha] = -3{\cdot}6°$.

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XVII.—*The Constitution of the Supposed* N-*Methylene-sulphurous Acid Derivative of Amines. Part I. Oxidation by an Alkaline Solution of Iodine.*

By GEORGE NEWBERY and MONTAGUE ALEXANDRA PHILLIPS.

DISODIUM 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene-*NN′*-dimethylenesulphite prepared by the action of excess of formaldehyde and sodium bisulphite on 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (salvarsan) is known by American chemists as "sulpharsphenamine" and its preparation and properties together with those of the corresponding acid have been described by Voegtlin and Johnson (*J. Amer. Chem. Soc.*, 1922, **44**, 2573) and by Christiansen (*ibid.*, 1923, **45**, 2182). The corresponding disodium 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene-*NN′*-dimethylenesulphoxylate is said (D.R.-P. 245756) to result on heating an aqueous suspension of salvarsan base with excess of sodium formaldehydesulphoxylate (rongalite) on the water-bath. When a similar method is applied with the replacement of rongalite by sodium formaldehydebisulphite, it appears that mono- or di-*N*-methylenesulphurous acid substitution products, or a mixture of these, result according to conditions of temperature and to the amount of the reagent present in excess. A reaction mixture so prepared at 60° with an excess of sodium formaldehydebisulphite, when filtered and poured into alcohol, yields a sodium salt which in its chemical behaviour as well as in its pharmacological action differs from that described by Voegtlin and Johnson (*loc. cit.*). A

aracteristic qualitative distinction is afforded by the action of N-hydrochloric acid, which causes the immediate precipitation of ie corresponding acid in the first case, but not in the latter, the leged acid * described by these authors as precipitated from the odium salt by glacial acetic acid being soluble both in water and i 2N-hydrochloric acid.

A chemical method for distinguishing substances of the type of eosalvarsan from sulpharsphenamine has recently been described y Elvove (*U.S. Public Health Reports*, June 12, 1925), and is based n the observation that the sulphur in the former is oxidised by odine in alkaline solution to sulphate and can be precipitated uantitatively as barium sulphate, whereas the combined sulphur in roducts of the latter type is not so oxidised. It is now shown that ie same distinction holds between the two sodium salts above entioned, the whole of the sulphur in the product of the action of odium formaldehydebisulphite on salvarsan base being oxidisable y iodine in alkaline solution.

It was found that although 4 : 4′-diaminoarsenobenzene yields ialogous products by similar methods, the sulphur in both is ompletely oxidised and is precipitated quantitatively as barium ilphate under the conditions laid down by Elvove.

These observations have led to the investigation of a number of nino-derivatives from this point of view. In each case the ydrochloride of the base was treated with two molecular pro-ortions of formaldehyde and of sodium bisulphite for each amino-oup and the total sulphur and the amount of sulphur oxidised ider the Elvove conditions were determined in aliquot portions of ie reaction mixture. In the case of those bases which gave ositive results the arsenic content (or in the case of 2-amino-ienol, the nitrogen content) of the solution was checked by timation in a further aliquot part. The results obtained are ibulated below.

Total S (g.) calculated from total S determination in aliquot portion = *a*.
Oxidised S (g.) calculated from S found in aliquot portion after oxidation under
vove conditions = *b*.

Substance (0·001 g.-mol.).	*a*.	*b*.	Non-oxidised S, *a*—*b*.	Atomic ratio, Non-oxidised S : As.
iiline	0·063	0·065	—	—
Aminophenol	0·065	0·046	0·019	—
Aminophenol	0·061	0·061	—	—
Aminophenol	0·060	0·061	—	—
Anisidine	0·064	0·062	—	—

* In our opinion the product precipitated was the sodium salt and not the id. The acid is apparently a strong one and its sodium salt is not decom-sed by acetic acid.

Substance (0·001 g.-mol.).	a.	b.	Non-oxidised S, a—b.	Atomic ratio, Non-oxidised S : As.
4-Aminophenylarsinic acid	0·064	0·064	—	—
3-Amino-4-hydroxyphenylarsinic acid	0·064	0·034	0·030	0·95
4-Amino-3-hydroxyphenylarsinic acid	0·063	0·030	0·033	1·03
4-Amino-2-hydroxyphenylarsinic acid	0·056	0·055	—	—
5-Amino-2-hydroxyphenylarsinic acid	0·059	0·059	—	—
2-Amino-4-hydroxyphenylarsinic acid	0·063	0·064	—	—
3-Amino-4-methoxyphenylarsinic acid	0·062	0·061	—	—
4-Aminoarsenobenzene	0·062	0·059	—	—
4 : 4′-Diaminoarsenobenzene *	0·128	0·135	—	—
3-Amino-4-hydroxyarsenobenzene	0·051	0·021	0·030	0·47
3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene	*0·135	0·067	0·068	1·00
	†0·202	0·131	0·071	1·11
	‡0·283	0·215	0·068	1·06
4 : 4′-Diamino-3 : 3′-dihydroxyarsenobenzene *	0·128	0·060	0·066	1·03
5 : 5′-Diamino-2 : 2′-dihydroxyarsenobenzene *	0·127	0·127	—	—
3 : 3′-Diamino-4 : 4′-dimethoxyarsenobenzene *	0·127	0·125	—	—

Two mol. proportions of formaldehyde were used in all cases except th marked * (4 mols.), † (6 mols.), and ‡ (8 mols.).

It will be seen that the combined sulphur is unoxidised by iodi in alkaline solution under the Elvove conditions only in the co pounds that contain an *o*-aminophenol group. Except in the ca of *o*-aminophenol, the atomic ratio of combined sulphur, so dete mined, to nitrogen approximates to unity. In confirmation of th experiments with salvarsan were made not only with four molecul proportions each of formaldehyde and sodium bisulphite but wi six and with eight proportions of each reagent. The ratio combined sulphur to nitrogen remained unaffected.

The conclusion is thus forced upon us that, at least from the bases which contain the *o*-aminophenol group, different a apparently isomeric sulphur acids are capable of being form according to whether the addition of sodium bisulphite is made the $:CH_2$ complex before or after condensation with the amin group of the base.

A common type of sulphur linkage which is not readily susceptil to oxidation (and is not, indeed, affected by oxidation under t Elvove conditions) is that of the sulphonic and sulphinic acids, *i.e.* direct linkage of carbon with sulphur. It might therefore assumed that sodium bisulphite reacts in a tautomeric manner in t two cases, thus :

$$(a)\quad {}^{H}_{H}\!\!>\!C{:}O + {}^{H{:}O}_{NaO}\!\!>\!S{:}O \longrightarrow {}^{H}_{H}\!\!>\!C\!<\!{}^{OH}_{O\cdot SO_2Na} + \cdot N\!<\!{}^{H}_{H}$$
$$\longrightarrow \cdot NH\cdot CH_2\cdot O\cdot SO_2Na \text{ (oxidised).}$$
$$(b)\quad \cdot N\!<\!{}^{H}_{H} + O{:}C\!<\!{}^{H}_{H} \longrightarrow \cdot N{:}C\!<\!{}^{H}_{H} + {}^{H}_{NaO}\!\!>\!S\!<\!{}^{O}_{O}$$
$$\longrightarrow \cdot NH\cdot CH_2\cdot SO_3Na \text{ (not oxidised).}$$

It would appear, however, that more than this is involved in the roblem, since, unlike compounds of the sulphonic or sulphinic acid ype, the sulphur derivatives here described as being resistant to xidation are very susceptible to the action of hydrolytic agents. ndeed the isolation in a state of purity of either di-sulphur acid in uestion presents difficulties which have so far proved insurmountble, so that direct proof of isomerism is at present lacking.

The evidence afforded by oxidation by alkaline iodine shows, we hink conclusively, the disubstituted nature of the sulpharsphenmine type of product. That the product of the action of two nolecules of sodium formaldehydobisulphite on salvarsan base is ot merely a mixture of the monosubstituted product with the xcess of the reagent is readily demonstrated by marked qualitative lifferences from such a mixture, differences which, however, lisappear after very mild acid hydrolysis.

Moreover, mild acid hydrolysis of a disubstituted product of the ype of sulpharsphenamine leads to the formation of a monoubstituted derivative of apparently the same type as that obtained y the action of sodium formaldehydebisulphite on the corresponding ase. In no case is such a product of hydrolysis found to contain ny appreciable amount of sulphur which remains unoxidised under he Elvove conditions.

Further, there seems no obvious reason why the proximity of he hydroxy-group should have such an effect on the mechanism of ombination. Ring formation of some kind would consequently ppear to be involved.

We have also to bear in mind that the commonly accepted view f the constitution of sodium formaldehydebisulphite and of sodium ormaldehydesulphoxylate as substances containing sulphur linked o carbon through oxygen has recently been called into question by Raschig (*Ber.*, 1926, **59**, 859). Binz (*ibid.*, p. 1695), on the other and, points out that many of the chemical properties of sodium ormaldehydesulphoxylate are better explained by assuming the C—O—S: formula. There appears to be good grounds for conidering both these compounds to be tautomeric in their chemical ehaviour.

We have thus at present no completely satisfactory explanation o offer for these observations, but it is hoped in future communi-

cations to examine more closely some individual cases of this apparent isomerism.

EXPERIMENTAL.

The methods used for the preparation of the following compounds call for some note.

4-Aminoarsenobenzene.—A solution of 4-aminophenylarsinic acid (4·4 g.) and phenylarsinic acid (4·0 g.) in saturated sodium carbonate solution (20 c.c.) was added to an ice-cold solution of magnesium chloride hexahydrate (10 g.) and sodium hyposulphite (40 g.) in water (600 c.c.). The solution was treated with charcoal, filtered, and heated for 2 hours at 30—40° (yield, 4 g.; 62%) (Found As, 46·8; N, 4·4. $C_{12}H_{11}NAs_2$ requires As, 47·0; N, 4·4%).

4-Aminoarsenobenzene was a light yellow powder insoluble in dilute acids and alkalis and in methyl alcohol and the usual organic solvents. It was converted by grinding with methyl-alcoholic hydrochloric acid into a *monohydrochloride*, which was insoluble in water (Found: As, 38·4; Cl, 9·5. $C_{12}H_{11}NAs_2,HCl,2H_2O$ requires As, 38·4; Cl, 9·1%). That this hydrochloride was not a mixture of 4:4′-diaminoarsenobenzene and arsenobenzene was shown by the fact that complete solution was obtained by suspension in water and treatment with formaldehyde and sodium bisulphite. No such solution could be obtained with arsenobenzene prepared by the reduction of phenylarsinic acid.

4:4′-Diaminoarsenobenzene was prepared in a similar manner (4-aminophenylarsinic acid, 9·2 g., in a slight excess of 2*N*-sodium carbonate; magnesium chloride hexahydrate, 5 g.; sodium hyposulphite, 40 g.; ice-water, 500 c.c.), the solution being finally heated for 1½ hours at 55—60° (yield, 4 g.; 56%) (Found: As 44·9; N, 8·6%). The product was insoluble in the theoretical amount of very dilute hydrochloric acid. On the other hand, the base prepared by hypophosphorous acid reduction (Kashima *J. Amer. Chem. Soc.*, 1925, **47**, 2207) was readily soluble in dilute hydrochloric acid, and the hydrochloride precipitated by the addition of 2*N*-hydrochloric acid in excess was still soluble in water after being dried in a vacuum (Found: As, 33·7; Cl, 15·9; N, 6·4 Calc. for dihydrate: As, 33·9; Cl, 16·0; N, 6·3%).

3-Amino-4-hydroxyarsenobenzene was prepared from 3-amino-4-hydroxyphenylarsinic acid (5·8 g.) and phenylarsinic acid (5 g.) by reduction with sodium hyposulphite (50 g.) and magnesium chloride hexahydrate (10 g.) in 500 c.c. of water for 2 hours at 60° (yield, 5 g.; 60%) (Found: As, 44·6; N, 4·1%). The yellow base was soluble in 2*N*-sodium hydroxide and, although not readily soluble in 2*N*-hydrochloric acid, was converted by suspension in methyl alcohol, addition of alcoholic hydrochloric acid and

finally of ether into a soluble hydrochloride (Found: As, 36·6; Cl, 8·8. Calc. for the monohydrochloride dihydrate: As, 36·8; Cl, 8·7%).

4-Amino-2-hydroxyphenylarsinic acid was prepared by a method essentially that since described by Hewitt and King (J., 1926, 822). No difficulty, however, was experienced in the isolation of the crude mixture of nitroethenyl-*o*-aminophenols when the nitration of ethenyl-*o*-aminophenol was carried out as follows: 100 g. of the fraction, b. p. 190—210°, from the preparation of ethenyl-*o*-aminophenol (Ladenburg, *Ber.*, 1876, **9**, 1524) were added to sulphuric acid (*d* 1·84; 500 c.c.), the temperature being allowed to rise to 60—70°. The cooled mixture was then nitrated at 10—20° by the slow addition (2½—3 hours) of a mixture of nitric acid (*d* 1·42; 60 c.c.) and sulphuric acid (*d* 1·84; 60 c.c.) with mechanical stirring. Completion of nitration was shown by the absence of the characteristic smell of the unchanged material on dilution with water. The bulk was poured on ice, washed free from acid, and dried at 90°.

The crude 5-*nitroethenyl*-o-*aminophenol* (111 g. = 90%; m. p. 145°) was very susceptible to hydrolytic agents and was not readily purified, repeated crystallisation from organic solvents such as acetic anhydride, alcohol, or acetone giving colourless, ill-defined needles of m. p. 150—151°, which was not raised by further crystallisation (Found: N, 15·8. $C_8H_6O_3N_2$ requires N, 15·7%). The product was not quite free from 4-nitroethenyl-*o*-aminophenol, since on hydrolysis as outlined below some 4-nitro-2-aminophenol always accompanied the main product.

The crude moist product from the above nitration was boiled with 400 c.c. of hydrochloric acid (*d* 1·16) until dissolved, sodium acetate was then added, and the precipitate thus formed was washed thoroughly with water, which removed the bulk of the 4-nitro-2-aminophenol. The residue of 5-nitro-2-aminophenol (m. p. 202° after crystallisation from hot water) was converted into 4-nitro-2-hydroxyphenylarsinic acid by the Bart method according to the details given by Lewis and Cheetham (*J. Amer. Chem. Soc.*, 1921, **43**, 2119) for *p*-carboxyphenylarsinic acid (yield, 62%) (Found: As, 28·4%). Reduction by the method of Jacobs, Heidelberger, and Rolf (*J. Amer. Chem. Soc.*, 1918, **40**, 1580) using ferrous sulphate then gave the same yield (84%) of 4-amino-2-hydroxyphenylarsinic acid as that recorded by Hewitt and King (*loc. cit.*) (Found: As, 32·2; N, 6·1%).

The corresponding arseno-base could not be obtained by the usual hyposulphite or hypophosphorous acid method owing to extremely ready de-arsenication with the production of polyarseno-compounds (compare Hewitt and King, *loc. cit.*).

5-Amino-2-hydroxyphenylarsinic Acid.—5-Nitro-2-hydroxyphenylarsinic acid prepared by Bart's method (*Annalen*, 1922, **429**, 97) from technical 4-nitro-2-aminophenol or by nitration of 2-hydroxyphenylarsinic acid (Keimatsu and Kakinuma, *J. Pharm. Soc. Japan*, 1925, No. 520, 2) was reduced according to the following details: To a solution of the acid (100 g.) in water (250 c.c.) and 2*N*-caustic soda (200 c.c.), ice (200 g.) was added, followed by sodium hyposulphite (240 g.), the temperature being below 10°. After 30 minutes' stirring, the solid was filtered off, washed, and purified as described by Christiansen for 3-amino-4-hydroxyphenylarsinic acid (*J. Amer. Chem. Soc.*, 1920, **42**, 2403). Yield, 50 g. (60%) (Found: As, 32·0%).

3-Hydroxy-4-aminophenylarsinic acid could not be readily obtained by Benda's method (*Ber.*, 1911, **44**, 3579) and was prepared as follows: 5-Nitroethenyl-*o*-aminophenol (10 g.) was slowly dusted into a boiling mixture of glacial acetic acid (5 c.c.), fine iron powder (12 g.), and water (30 c.c.). The hot mixture was made alkaline to phenolphthalein with 2*N*-sodium carbonate and diluted to 100 c.c. with boiling water. The combined filtrate and washings from the iron oxides were concentrated to 50 c.c. under reduced pressure; on cooling, *5-aminoethenyl-o-aminophenol* (4 g.; 50% yield) crystallised in diamond-shaped plates, moderately easily soluble in cold water and readily soluble in dilute mineral acids. Purified by reprecipitation by sodium acetate from hydrochloric acid solution, it had m. p. 147° (Found: N, 18·8. $C_8H_8ON_2$ requires N, 18·9%). Its orientation was confirmed by the fact that hydrolysis by boiling 2*N*-hydrochloric acid, followed by acetylation, led quantitatively to an acetyl derivative, m. p. 260° (Found: N, 13·7%), identical with 2 : 5-diacetamidophenol prepared by the reduction of pure 5-nitro-2-aminophenol, followed by acetylation (Kehrmann and Betsch, *Ber.*, 1897, **30**, 2099).

4-Acetamido-3-hydroxyphenylarsinic acid was made from the foregoing aminoethenyl derivative by the Bart method; the yield was poor (10%). The compound crystallises in characteristic needles, and is insoluble in cold water and in dilute mineral acids (Found: As, 27·2; N, 5·1%). On hydrolysis with hot 20% sodium hydroxide solution, followed by acidification with acetic acid, it gave 4-amino-3-hydroxyphenylarsinic acid in 90% yield; this, purified by the Christiansen method (*loc. cit.*), crystallised in short, stout prisms (Found: As, 32·4; N, 6·0%). It differed from 3-amino-4-hydroxyphenylarsinic acid in giving a green instead of a red coloration with chromic acid and in its lower basicity. Thus at comparable dilutions 1 mol. of 3-amino-4-hydroxy-, 2-amino-4-hydroxy-, and 4-amino-3-hydroxy-phenylarsinic acids respectively required

pproximately 4, 8, and 12 mols. of hydrochloric acid for complete olution. The same properties were shown by the product obtained om 5-aminobenzoxazolone by the Bart method, followed by kaline hydrolysis (Amer. Patent 1539799/1924).

4 : 4′-Diamino-3 : 3′-dihydroxyarsenobenzene was prepared by a ight modification of the method suggested by Benda (*loc. cit.*). he alkaline solution of the purified β-naphthol dye was treated at –5° with sufficient sodium hyposulphite to discharge the colour of ie solution, which was then saturated with carbon dioxide. After moval of 1-amino-2-naphthol, the filtrate was reduced with a 50% cess of sodium hyposulphite for 2 hours at 60°.

The arseno-compound was converted into its hydrochloride in iethyl alcohol and precipitated by ether. It was readily soluble in ater (Found: As, 31·0; N, 5·7; Cl, 14·0. Calc. for dihydrate: s, 31·6; N, 5·9; Cl, 14·9%).

2-Amino-4-hydroxyphenylarsinic acid was prepared according to ie scheme outlined by Fourneau (*Ann. Inst. Pasteur*, 1923, **37**, 76). 3-Nitro-4-aminophenol gave by the Bart method 2-nitro-4-ydroxyphenylarsinic acid (50%), which on reduction (Jacobs, eidelberger, and Rolf, *loc. cit.*) gave the required amino-acid ield, 80%) (Found: As, 32·4; N, 6·1%).

The corresponding arseno-base, like that from 2-hydroxy--aminophenylarsinic acid above, was not readily obtained by the rdinary methods of reduction, owing to the readiness with which e-arsenication occurred.

General Method of Examination.—The hydrochloride (0·001 g.-iol.) of the base under examination was dissolved in water (5 c.c.) r alternatively an equivalent amount of the base dissolved in the iinimum of hydrochloric acid was made up to about 5 c.c. 4% ormalin solution (1·5 c.c., *i.e.*, 2 mols. per 1 at. of amino-nitrogen) *as added and then after the lapse of 60 seconds* * *a solution of* odium bisulphite (0·208 g.; 2 mols. per 1 at. of amino-nitrogen). n certain cases, particularly those of arseno-compounds, precipittion of a yellow product ensued which rapidly re-dissolved on iaking. After 30 minutes, the solution so obtained was diluted to 00 c.c. and aliquot portions were taken for the determinations ctailed below.

The above amounts are those for mono-acid bases; the quantities f the reagents were doubled for the di-acid bases. For 3 : 3′-di-mino-4 : 4′-dihydroxyarsenobenzene, the proportions of the re-gents were varied, 4, 6, and 8 mols. each of formaldehyde and of

* In the case of 3-amino-4-hydroxyarsenobenzene only 15 seconds were lowed, as otherwise the subsequent dissolution of the solid precipitated on ie addition of the sodium bisulphite was difficult to accomplish.

sodium bisulphite being employed in three separate experiments. As the ratio of arsenic to non-oxidisable sulphur remained approximately constant, it was assumed that 2 mols. of the reagents per 1 at. of amino-nitrogen was a sufficient excess in all cases for the completion of the reaction.

Nitrogen was determined, in the case of the examination of 2-aminophenol, by the Kjeldahl method, 25 c.c. of the solution being employed.

Arsenic was estimated in 25 c.c. of the solution by the ammonium persulphate method described by one of us (J., 1925, **127**, 1751).

Total sulphur was determined in 25 c.c. by evaporation and fusion with a eutectic mixture of sodium and potassium carbonates (4 parts) and potassium nitrate (1 part), followed by precipitation of the sulphur as barium sulphate. An experimental correction for adsorbed salts was applied (compare Christiansen, *J. Amer. Chem. Soc.*, 1922, **44**, 853). This determination was made as a check on the amount of sulphur introduced as sodium bisulphite.

Oxidised sulphur. 50 C.c. of the solution were estimated by Elvove's method (*loc. cit.*), excess of $0{\cdot}1N$-iodine (75 c.c.) being added, followed by 10 c.c. of $2N$-sodium hydroxide. After 5 minutes 11 c.c. of $2N$-hydrochloric acid were added and the excess of iodine was removed by the addition of a $0{\cdot}05M$-sodium arsenite solution (50 c.c.). When the solution was completely decolorised, it was further acidified by addition of $2N$-hydrochloric acid (10 c.c.) and the sulphate in the solution estimated in the usual manner as barium sulphate.

Sodium 4 : 4′-*Diaminoarsenobenzenedimethylenesulphite* (*A*).—Difficulty was experienced in attempts to repeat the details of the method of Kashima (*J. Amer. Chem. Soc.*, 1925, **47**, 2208), the product of the action of formalin upon 4 : 4′-diaminoarsenobenzene after isolation being incompletely soluble on the addition of sodium bisulphite. It was found preferable to use a method similar to that of Christiansen (*loc. cit.*). 4 : 4′-Diaminoarsenobenzene (4 g.) made according to Kashima (*loc. cit.*) was suspended in water (30 c.c.) and dissolved by the cautious addition of $2N$-hydrochloric acid. Formalin (40%, 2·5 c.c.) and, after the lapse of 60 seconds, sodium bisulphite (3·25 g.) in water (5 c.c.) were then added to the suspension of the formaldehyde compound. Solution was quickly effected, and the mixture was then shaken with charcoal, filtered, and precipitated in 500 c.c. of spirit. The product, after being washed with spirit and dried in a vacuum over sulphuric acid (yield, 5 g.), was dark yellow and soluble in water. A 10% solution was not precipitated by an equal volume of $2N$-hydrochloric acid even after some hours' standing, nor did it decolorise a hot solution

of indigo-carmine (Found : As, 25·3 ; N, 4·0 ; total S, 12·8 ; S by the Elvove oxidation method, 13·1%. As : N : S = 1 : 0·87 : 1·19).

Sodium 4 : 4'-Diaminoarsenobenzenedimethylenesulphite (B).—The moist base obtained by hypophosphorous acid reduction of 4-aminophenylarsinic acid (8 g.) was ground with sodium formaldehydebisulphite (5 g.) and water (25 c.c.). The mixture was heated at 60° for 2½ hours, and the turbid solution filtered through kieselguhr and precipitated by pouring into spirit (500 c.c.). The light yellow product was filtered off, washed, and dried as before (3 g.). (Found : As, 25·2 ; N, 4·7 ; total S, 10·1 ; S by the Elvove oxidation method, 10·3%. As : N : S = 1 : 1·0 : 0·94). It was readily soluble in water. A 10% solution did not decolorise hot indigo-carmine solution, but was precipitated after a just perceptible delay by the addition of an equal volume of 2*N*-hydrochloric acid.

The acid obtained was readily soluble in dilute alkali hydroxide or carbonate : its gelatinous character and ready oxidation in air precluded satisfactory analysis.

Sodium 3 : 3'-Diamino-4 : 4'-dihydroxyarsenobenzene-NN'-*dimethylenesulphite (A).*—A specimen prepared according to Christiansen (*loc. cit.*) gave the following figures : As, 18·0 ; N, 3·3 ; total S, 13·9 ; S by the Elvove oxidation method, 5·3 ; unoxidised S by difference, 8·6%. Atomic ratio, As : N : unoxidised S = 1 : 0·98 : 1·12.

Hydrolysis of the sodium salt. In a solution of 5·0 g. in water (15 c.c.) 2*N*-hydrochloric acid (10 c.c.) caused *no* precipitation (compare preparation B described below). The mixture was warmed at 60—70° until a sample on cooling deposited a yellow, amorphous solid (5—7 minutes). The whole was cooled and the solid was filtered off after 10 minutes, washed with water, and dried in a vacuum over sulphuric acid (yield, 2·5 g.). The product was freely soluble in alkali hydroxide or carbonate and the solution so obtained was readily precipitated by 2*N*-acetic acid or 2*N*-hydrochloric acid (Found in three preparations : As, 31·0, 31·1, 31·4 ; N, 5·55, 5·95, 5·4 ; total S, 8·0, 7·65, 7·7 ; S by the Elvove oxidation method, 7·2, 6·85, 7·5 ; unoxidised S by difference, 0·8, 0·7, 0·2%. Mean atomic ratio, As : N : total S = 2 : 1·92 : 1·16. $C_{13}H_{14}O_5N_2SAs_2$ requires As, 32·6 ; N, 6·1 ; S, 7·0%).

Sodium 3 : 3'-Diamino-4 : 4'-dihydroxyarsenobenzene-NN'-*dimethylenesulphite (B).*—3 : 3'-Diamino-4 : 4'-dihydroxyarsenobenzene obtained from 3-amino-4-hydroxyphenylarsinic acid (50 g.) by the usual hyposulphite reduction method was, without being dried, ground to a paste with a solution of sodium formaldehydebisulphite (30 g.) in water (250 c.c.). The mixture was heated at 60° until solution was effected (about 3 hours), filtered, and precipitated by pouring it into 3 litres of spirit. The product was washed and dried

in a vacuum (yield, 37 g.) (Found: As, 25·2; N, 4·7; total S, 10· S by the alkaline oxidation method, 10·3%. As:N:S = 1:1·0:0·9] A solution in water was not precipitated by an equal volum of 2*N*-acetic acid and did not decolorise a hot indigo-carmi solution.

A similar solution, treated with 2*N*-hydrochloric acid (2 parts gave after a few seconds' delay a voluminous, light yellow precipita which remained soluble in water (as shown by dilution) for a peri of some minutes at the ordinary temperature and for 30—60 minut at 0°. The insoluble acid formed on standing was apparent identical with that described below under the heading of hydrolysi All attempts to isolate the soluble acid for analysis proved abortiv even when precipitation, filtration, and washing with *N*-hydr chloric acid were carried out at 0°, the product becoming insolub when dry. Figures obtained for the insoluble acid in all cas indicated a monosubstituted product.

Hydrolysis of sodium salt. The above product (7 g.) was dissolve in water (20 c.c.), 2*N*-hydrochloric acid added, and the mixture heate in the water-bath. The acid which separated quickly redissolve and sulphur dioxide was evolved. On cooling, a dark yello product separated which was washed and dried to constant weight i a vacuum (yield, 3 g.) (Found: As, 33·0; N, 5·6; total S, 7·1; S b the Elvove oxidation method, 6·5. Calc.: As, 32·6; N, 6·1; S 7·0%).

The product was readily soluble in dilute caustic alkali or ca bonate solution and the solution so obtained was readily precipitate by 2*N*-acetic acid or hydrochloric acid and did not decolorise h indigo-carmine solution.

*Sodium 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene-*N*-monomethy enesulphite* was prepared from 3 : 3'-diamino-4 : 4'-dihydroxyarsen benzene (6·8 g.) which was heated with a solution of sodium form aldehydebisulphite (2·5 g.) in water (30 c.c.) at 60° with mechanic stirring until solution was almost complete (1—2 hours). Aft filtration through a kieselguhr bed, the product was precipitate in an excess of alcohol, filtered, washed, and dried in a vacuum. I was readily soluble in water, and the corresponding acid was pr cipitated by dilute acetic acid, even in presence of excess of sodiu formaldehydebisulphite, and by dilute mineral acids. The solutio did not decolorise a hot indigo-carmine solution (Found: As, 31·2 N, 5·3; total S, 7·1; S by the alkaline iodine method, 7·0% As : N : S = 2 : 1·84 : 1·06).

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XVIII.—*The Salting-out Effect. Influence of Electrolytes on the Solubility of* m-*Cresol in Water.*

By John Stanley Carter and Richard Kenneth Hardy.

Measurements of the solubilities of certain non-electrolytes in solutions of various salts have shown that, provided interaction between non-electrolyte and salt be excluded, the relation between the solubility s and the salt concentration c is represented by the exponential equation $s = s_0e^{-kc}$, where s_0 has a value equal to, or approximating to, the solubility in the pure solvent, and k is a constant which measures the salting-out effect of the salt (Setschenow, *Z. physikal. Chem.*, 1889, **4**, 117; Dawson, *J. Soc. Chem. Ind.*, 1920, **39**, 151T; Thorne, J., 1921, **119**, 262; Linderström-Lang, *Compt. rend. Trav. Lab. Carlsberg*, 1924, **15**, 4; Carter, J., 1925, **127**, 2861). When the salts are replaced by the corresponding acids, the above relationship is no longer valid, the solubility of the non-electrolyte often varying in a very complex manner with increasing concentration of acid (Manchot, Jahrstorper, and Zepter, *Z. anorg. Chem.*, 1924, **141**, 45; Carter, *loc. cit.*).

The measurements now recorded relate to the effects produced by the chlorides and sulphates of sodium and magnesium, the corresponding acids, and mixtures of phosphoric acid and sodium phosphate on the solubility of *m*-cresol in water at 25°. The *m*-cresol used had m. p. 9·5° and was obtained by distillation of a sample which had undergone a rigorous process of purification and in which the only impurity appeared to be water. Precautions were taken to ensure saturation and efficient filtration. *m*-Cresol was determined by the bromide–bromate method (Fox and Barker, *J. Soc. Chem. Ind.*, 1920, **39**, 169T). Electrolytes were determined by standard methods. The solubility of *m*-cresol in water at 25° was found to be 2·27 g./100 g. of solution, or 3·87 mols. per 1000 mols. of water, duplicate experiments giving exactly the same figure.

In the two following tables c represents the number of equivalents of electrolyte per 1000 mols. of water. The solubility of *m*-cresol is expressed in the same way, s being the measured value and s' the value calculated from the exponential equation, which was put into the form $\log s' = \log s_0 - k'c$, the value of the constant k' being given by the slope of the line on plotting $\log s$ as a function of c. On constructing such graphs from the data for the four salts investigated, it was found that the resulting lines did not cut the solubility axis at a point corresponding with the solubility of *m*-cresol in pure water, but at points corresponding with a somewhat lower

value. Differences between the measured and extrapolated valu for the solubility in the pure solvent were observed by Dawson wi phenol and by Thorne with ether. Extrapolated values s'_0 ha been used in the calculation of the s' values given, which agr satisfactorily with the observed values (see Table I).

TABLE I.

c.	s.	s'.	c.	s.	s'.
		Sodium chloride, $s'_0 = 3·61$, $k' = 0·0101$.			
8·20	3·03	2·99	45·84	1·25	1·25
15·89	2·54	2·50	54·38	1·04	1·02
27·09	1·89	1·92	68·26	0·73	0·74
42·19	1·38	1·36	89·80	0·50	0·45
		Magnesium chloride, $s'_0 = 3·61$, $k' = 0·00815$.			
12·77	2·87	2·84	55·49	1·28	1·28
26·87	2·19	2·18	61·95	1·11	1·13
42·65	1·59	1·62	66·59	1·04	1·03
		Sodium sulphate, $s'_0 = 3·80$, $k' = 0·01405$.			
6·08	3·08	3·12	32·43	1·36	1·33
14·22	2·39	2·40	41·88	0·97	0·98
16·29	2·24	2·24	62·13	0·52	0·51
		Magnesium sulphate, $s'_0 = 3·80$, $k' = 0·0119$.			
6·86	3·13	3·15	29·97	1·69	1·67
14·22	2·58	2·58	47·74	1·00	1·03
24·23	1·97	1·96	80·44	0·37	0·42

Although the solubility of *m*-cresol in solutions of hydrochlo and of sulphuric acids (Table II) decreases in a regular manner wi increasing concentration of acid, the exponential law is not obeye

TABLE II.

		Hydrochloric acid.				
c	9·62	20·22	40·83	49·09	66·40	77·0
s	3·39	3·17	2·83	2·80	2·71	2·6
		Sulphuric acid.				
c	8·60	18·11	38·84	52·35	61·86	83·3
s	3·39	3·09	2·57	2·34	2·14	1·8

moreover, the solubility is greater than in solutions of the corr sponding salts, and, as in the case of the salts, the salting-o efficiency of the sulphate ion is greater than that of the chloride ic

In order to see how the magnitude of the solubility loweri produced by an acid electrolyte is altered by the progressive placement of the dissociable hydrogen atoms by metal aton measurements were made of the solubility of *m*-cresol in phospho acid–sodium phosphate mixtures characterised by the approxima constancy of the concentration of phosphate ion. Actually t concentrations c of these solutions varied between 0·997 and 1·024 Assuming that over this small range of concentration-differences t

solubility lowering is proportional to concentration, the values of $l = 100(s_0 - s)/s_0c$ were calculated. The value of l thus represents the percentage lowering of the solubility produced by an electrolyte which may be regarded as possessing the formula $H_{3-x}Na_xPO_4$ at a concentration of $1 \cdot 0 N_w$. The data are presented in Table III.

TABLE III.

Solution.	A.	B.	C.	D.	E.	F.
x	0·0	0·512	1·011	1·512	2·008	2·845
l	10·5	18·6	25·1	29·9	33·3	−65·4

The greatly increased solubility of *m*-cresol in solution F is due to its reaction with the alkali present to form sodium *m*-tolyloxide. Solution E had a slightly alkaline reaction (p_H 9), but in view of the extremely small dissociation constant of *m*-cresol, there can have been practically no formation of tolyloxide. Neglecting the result for the most alkaline solution, a smooth curve is obtained on plotting l against x. The value of the ratio $\Delta l/\Delta x$ decreases as x increases.

The fact that the solubility lowerings produced by acids are much smaller than those produced by the corresponding salts shows that the salting-out powers of ions of the same valency do not necessarily increase with decreasing size of the ions, although this is usually the case, as Glasstone, Dimond, and Jones have pointed out in reference to the effect of various salts on the solubility of ethyl acetate (J., 1927, 2935).

Our thanks are due to the Government Chemist, Sir Robert Robertson, F.R.S., for providing facilities for the work and for permission to publish these results, and to Dr. J. J. Fox for his continued interest and advice, and for his kindness in supplying us with a quantity of pure *m*-cresol.

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XIX.—*The Velocity Coefficient for Bimolecular Reactions in Solution.*

By RONALD G. W. NORRISH and FREDERICK F. P. SMITH.

THE application of the kinetic molecular theory to the problem of chemical reactivity, which has met with considerable success in the case of bimolecular reactions in gases at the hands of Hinshelwood and his co-workers, has given us the important concept of kinetic activation which would appear to be of far-reaching and funda-

mental importance to the understanding of the kinetics of dark reactions.

The velocity coefficient k of a bimolecular gaseous reaction can be calculated (Lewis, J., 1918, **113**, 471) by means of the equation

$$k_T = m \times 114 \times 10^{21} \left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 \sqrt{u_1^2 + u_2^2} \cdot e^{-E/RT} \qquad (1)$$

where σ_1 and σ_2 are the molecular diameters, u_1 and u_2 are the velocities of the reacting molecules, m is the number of resultant molecules formed at each collision, and E is the energy of activation obtained from the temperature coefficient of the reaction. The object of the present paper is to examine the above equation in the case of non-ionic reactions in solution.

For this purpose, reactions of the simplest possible type are required taking place in a non-ionising solvent with regular and measurable velocities. The test may then be carried out either (1) by comparing two closely similar reactions in the same solvent in order to eliminate effects of solvation, or (2) by finding an expression for the number of effective collisions per second between the dissolved reactants in terms of the critical increment determined from the temperature coefficient, and comparing the results given by the expression with the experimentally observed velocity. Both these methods have been adopted in the present paper.

No suitable reactions could be found in the literature to provide data for the present investigation. A careful study has therefore been made of the velocities and temperature coefficients of two reactions which were considered to approach closest to our ideal requirements—the interactions of trimethylamine with *m*- and with *p*-nitrobenzyl chloride in carbon tetrachloride and benzene solutions.

EXPERIMENTAL.

The *m*- and *p*-nitrobenzyl chlorides after recrystallisation from petroleum ether (b. p. 40—60°) melted at 45·5° and 72·5°, respectively, and gave correct analyses. The trimethylamine was obtained from its hydrochloride by treatment with concentrated potassium hydroxide solution and warming, the evolved gas being passed through three soda–lime tubes and absorbed in the cooled solvent. The strength of the solution was obtained by titration with $N/10$-hydrochloric acid, a mixture of methyl-orange and sodium indigotinsulphonate being used as indicator. The solvents, benzene and carbon tetrachloride, were purified in the usual manner, the thiophen-free benzene being frozen and distilled from phosphoric oxide, and the carbon tetrachloride washed with soda and distilled from fused calcium chloride.

The velocity measurements were carried out in nine boiling tubes. These were drawn out and placed in a bath of ice, and 10 c.c. of nitrobenzyl chloride solution and 10 c.c. of base were placed in each tube, which was then quickly sealed off and placed in the thermostat, the timing being started from this point.

The method of analysis varied with the solvent. In the case of benzene, the tube was opened and the contents were washed into a conical flask containing dilute nitric acid to stop the reaction, and a known quantity of silver nitrate solution. The whole was shaken with a considerable quantity of ether for about one minute in order to coagulate the silver chloride. The excess of silver nitrate was titrated with ammonium thiocyanate in the usual way.

Two thermostats were run side by side, and solutions for velocity measurements in each of them were made from the same stock solution, the reactions with the *m*- and *p*-isomerides being conducted at each temperature simultaneously. The strength of the silver nitrate solution was 0·04986*N*; *a* represents the concentration of the amine, *p* that of *p*-nitrobenzyl chloride, and *m* that of *m*-nitrobenzyl chloride. Tables I and II are specimens of the complete results with benzene as solvent, whilst Table III gives a summary of the results, the concentrations *a*, *m*, and *p* being expressed as normalities.

The logarithm of the velocity coefficient for both the *m*- and the *p*-nitrobenzyl chloride reactions was plotted against the inverse of the absolute temperature. In each case a straight line was obtained, from which Table IIIA was compiled.

TABLE I.

p-Nitrobenzyl chloride and trimethylamine at 30°.

$p = 0{\cdot}08231N$; $a = 0{\cdot}1276N$.

Time (mins.).	$AgNO_3$ (c.c.).	*x*.	$k\,.\,10^3$.	Time (mins.).	$AgNO_3$ (c.c.).	*x*.	$k\,.\,10^3$.
1246	8·92	0·0224	2·19	2686	15·22	0·03794	2·18
1290	9·16	0·02283	2·18	3924	18·90	0·04712	2·19
2480	14·71	0·03667	2·23	3955	18·92	0·04718	2·17
2661	15·22	0·03794	2·20	3983	19·05	0·04794	2·19
							Mean 2·19

TABLE II.

p-Nitrobenzyl chloride and trimethylamine at 25°.

$p = 0{\cdot}08231N$; $a = 0{\cdot}1280N$.

Time (mins.).	$AgNO_3$ (c.c.).	*x*.	$k\,.\,10^3$.	Time (mins.).	$AgNO_3$ (c.c.).	*x*.	$k\,.\,10^3$.
2776	13·03	0·03248	1·65	5614	19·38	0·04832	1·60
2806	13·05	0·03253	1·63	5661	19·40	0·04837	1·59
3897	16·00	0·03988	1·62	5676	19·44	0·04846	1·59
3934	16·05	0·04000	1·62	5728	19·47	0·04854	1·58
3955	16·07	0·04005	1·61				Mean 1·61

TABLE III.

Temp.	*a*.	*p*.	*m*.	Limits of $k \times 10^5$.	$k \times 10^5$
35°	0·0842	0·1172	—	305—293	301
35	1·1319	—	0·07787	217—212	214
30	0·1276	0·08231	—	223—217	219
30	0·1290	—	0·08130	163—152	158
25	0·1280	0·08231	—	165—158	161
25	0·1301	—	0·08130	119—112	115

TABLE IIIA.

Reactant.	k_{25}.	k_{35}.	k_{35}/k_{25}.	E.
p-Nitrobenzyl chloride	0·00161	0·00298	1·851	11,210
m- ,, ,, ...	0·00115	0·00214	1·861	11,320

When carbon tetrachloride was used as solvent, consiste velocity coefficients could not be obtained. When an aqueo suspension of silver chloride, carbon tetrachloride, and ether shaken, an unmanageable emulsion results, but this difficulty w overcome by filtering off part of the silver chloride and the wh of the carbon tetrachloride through a wet Swedish filter-pa before adding the ether. The reason for the irregularity has n been elucidated, but it may be due to the formation of a compl between trimethylamine and carbon tetrachloride, since a wh solid is deposited from 0·3*N*-solutions of the amine in carb tetrachloride.

Discussion of Results.

The main difficulties to be overcome in applying equation (1) test the kinetic molecular hypothesis of reaction in solution are d to the uncertainty of the effect of the solvent upon the concentrati and diameter of the dissolved molecules.

The Calculation of ($E_1 - E_2$) *for Two Similar Reactions*.—Th difficulties can, however, be *partly* eliminated by comparing t above two closely similar reactions in the same non-polar solve If we take the same concentrations of reactants in each case, it probable that they will suffer the same number of molecular e counters, since no great difference in solvation or molecular veloci is to be imagined between the two isomerides in such a non-pol solvent as benzene. By applying equation (1) to the two reaction we can therefore eliminate the σ and u terms by division, and obta the relationship $k_1/k_2 = e^{-E_1/RT}/e^{-E_2/RT}$ or $(E_1 - E_2)/RT = \log_e k_2/k$ Hence the difference between the critical increments can be ca culated from the ratio of the velocity coefficients, and compared wi that obtained directly from a measurement of the temperatu coefficients of the reactions.

If the conditions described above for making the rôle of th solvent merely one of a medium for the reaction are successful, the

; no reason why E_1, E_2, and $(E_1 - E_2)$ should not be obtained with ome accuracy. In the equation $k_1/k_2 = e^{-(E_1-E_2)/RT}$, small changes 1 $E_1 - E_2$ are considerably magnified in k_1/k_2, and hence a slight rror in k_1/k_2 will hardly influence $E_1 - E_2$. Similarly, in the quation $\log_e k_{T_2}/k_{T_1} = E/R \,.\, (1/T_1 - 1/T_2)$, a small experimental rror in k_{T_2}/k_{T_1} will have but little effect on E.

In Table IV, the results obtained in the present paper are comared with those obtained by Olivier (*Rec. trav. chim.*, 1923, **42**, 16) for the hydrolysis of various benzyl halides with a mixture of qual parts of water and alcohol, and by Conant (*J. Amer. Chem. oc.*, 1925, **47**, 488) for the reaction of various benzyl chlorides with otassium iodide in acetone solution. In both these cases, the olvent was of a highly polar character, and in the second case one f the reactants was an ion. For these reasons, and also for reasons f steric hindrance where the reactions of *o*- and *p*-isomerides are ompared, we should not expect the same close agreement between he two methods of determining $(E_1 - E_2)$ as that to be obtained hen precautions are taken to eliminate serious errors due to ifferences of solvation and steric hindrance in the isomeric subances employed. This, indeed, is seen to be the case, for in the resent reaction where these disturbing effects have been reduced) a minimum, the concordance between the two methods of alculating $(E_1 - E_2)$ is close, the two values differing only by 0 cals., while in the other cases cited the divergences vary from 60 cals. to 1660 cals.

TABLE IV.*

	E_1 and E_2 from temp. coeff.	$E_1 - E_2$ from temp. coeff.	$E_1 - E_2$.
· and *p*-Nitrobenzyl chlorides + trimethylamine	11,320 / 11,210	110	200
· and *p*-Bromobenzyl chlorides + KI	19,140 / 17,970	1,170	−250
· and *o*-Chlorobenzyl chlorides + KI	18,330 / 17,610	720	160
·Chloro-*p*- and ·*o*-xylenes + alcohol–water	20,460 / 19,860	600	−550
·Chloro-*p*- and ·*m*-xylenes + alcohol–water	20,460 / 20,230	230	−1430

The Calculation of the Velocity Coefficient, k.—We will now consider he more general problem of the calculation of the velocity coefficient f a non-ionic reaction in non-polar solution, as Lewis (*loc. cit.*) and

* Since writing this paper, we have found that Peacock (*J. Physical Chem.*, 927, **31**, 535), working from a different point of view, calculated $E_1—E_2$ by he two methods given in the text for certain reactions studied by himself nd by Holleman. Neither of the sets of reactions was carried out in nonolar solvents, and the reactions studied by Peacock give velocity coefficients hich vary with the initial concentration of the reactants.

Hinshelwood (J., 1923, **123**, 2730; 1924, **125**, 184) have done for *gaseous systems.*

The expression giving the number of collisions per c.c. per second between two gases containing n_1 and n_2 molecules per c.c. is

$$Z = \pi\left(\frac{\sigma_1 + \sigma_2}{2}\right)^2 n_1 n_2 \sqrt{u_1^2 + u_2^2} \quad . \quad . \quad . \quad (2)$$

where the symbols have the same significance as in (1). This expression, as Christiansen (*Z. physikal. Chem.*, 1924, **113**, 35) has suggested, will apply also to the case of the collisions between two solutes, but it will be subject to correction for the true values of σ_1 and n_2 which are somewhat affected by the presence of the solvent.

It has been suggested (Lewis, " A System of Physical Chemistry," Vol. III, p. 225) that the number of collisions in the case of a bimolecular reaction in solution can be calculated from the diffusion coefficient of the bodies involved. It is possible to show, however, that we obtain by this means the same result as is given by equation (2). If Δ is the mean displacement in a given direction in time τ, then the diffusion coefficient is given by $D = \frac{1}{2}\Delta^2/\tau = \frac{1}{2}\Delta v$, where v is the mean velocity of displacement. If τ is made equal to the time between successive collisions between solute molecules, Δ becomes their " linear " mean free path. Hence the number of collisions per second will be given by v/Δ. Now the actual path of the solute molecule between collisions is irregular owing to collisions with the solvent; it will be described with a mean velocity equal to the average thermal velocity of agitation, and the total distance travelled will be L, approximately equal to the mean free path L in a gas at the same concentration. Now since Δ is the algebraic sum of the resolved parts of the irregular path L in a given direction, and the resultant mean velocity v is obtained by resolving and summing the thermal velocity over the path L in the same way, $v/\Delta = u/L =$ number of collisions calculated from gas theory. Calculation by the help of the diffusion theory, is, however, rendered impossible, since there is no way of obtaining Δ independently, the Clausius equation being inadmissible. We shall therefore use equation (2) in the calculation of the number of collisions in solution allowing for the following secondary effects of the solvent :

(1) The free space, and therefore the concentration of the solute, will be affected by the actual volumes occupied by solvent molecules. This volume, s, can be determined from the critical data of the solvent or from the Clausius–Mossotti theory of dielectrics, and is of the order of 24 c.c. per g.-mol. for benzene. If V is the molecular volume of the solution, the effective concentration of a solute in benzene is thereby increased by the factor $V/(V - s) = 1{\cdot}26$.

(2) Solvation. The molecular diameters of a number of solutes ı various organic solvents have been calculated by the Stokes–]instein diffusion expression by means of data obtained by Thovert 4nn. *Physique*, 1914, **2**, 369), Oholm (*Medd. K. Vetenskapsakad. Vobel.-Inst.*, **2**, No. 24 and No. 26), Dummer (*Z. anorg. Chem.*, 920, **109**, 31), and Miller (*Proc. Roy. Soc.*, 1924, *A*, **106**, 124), and hey have been found to vary little from solvent to solvent, and also o be of the same order as the value determined for gases by Rankine. n subsequent calculations we have taken the value of the molecular iameter to be 4×10^{-8} cm. for all the cases considered.

The Discrepancy between the Observed and the Calculated Values of he Velocity Coefficient.—The experimentally determined values of he critical increment, E, now enable us to calculate the velocity oefficient by equation (1) corrected for solution as above :

$$k = 114 \times 10^{21}[V/(V - s)]^2 \times 16 \times 10^{-16}\sqrt{u_1^2 + u_2^2} \cdot e^{-E/RT}$$

]aking the critical increment E as 11,200 cals., we obtain the velocity oefficient at 30° for the reaction between *p*-nitrobenzyl chloride and rimethylamine as $1{\cdot}2 \times 10^5$, whereas that determined experinentally is 0·00219.

The reason for this large discrepancy must undoubtedly be bound ıp with the nature of the liquid state : in the solvent, the mean free ›ath is of the same order as the molecular diameter. Nearly every ollision between potentially reactant solute molecules must thereore of necessity partake of the nature of a ternary collision at least, a which the third body is a solvent molecule. The energy of ollision must therefore be divided between three (at least) instead f only two molecules, and the solvent, according to its molecular tructure, may take up a large or small quantity of the energy which vould otherwise lead to chemical reaction. It may thus happen hat the number of fruitful contacts between molecules is small com›ared with the number calculated from the simple bimolecular heory. To allow for this deactivating action of the solvent we may eintroduce the probability factor P into the velocity-coefficient quation; P therefore represents the fraction of effective to total ollisions taking place between molecules possessing the required nergy of activation, and is equal to $0{\cdot}00219/1{\cdot}2 \times 10^5 = 1{\cdot}9 \times 10^{-8}$ for the above reaction.

Other Reactions.—It appeared of interest to see how P varies from olvent to solvent, or in the same solvent for two similar reactions.]he following reactions have been employed :

I. The reactions studied above.

II. The reaction between bromoacetophenone and aniline,

$$C_6H_5{\cdot}NH_2 + CH_2Br{\cdot}CO{\cdot}C_6H_5 = (C_6H_5{\cdot}NH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5)Br,$$

studied by Cox (J., 1921, **119**, 142) in several solvents and at more than one temperature.

III. The reaction between pyridine and allyl bromide, $C_5H_5N + C_3H_5Br = (C_5H_5N{\cdot}C_3H_5)Br$, studied by Hawkins (J., 1922, **121**, 1170).

The result of these calculations is shown in Table V. The volume occupied by the molecules in 1 g.-mol. of solvent, S, is taken as one-quarter of the volume at absolute zero, except in the cases of butyl alcohol and chloroform, where it is obtained from the Clausius–Mossotti theory of dielectrics.

TABLE V.

	Reaction and solvent.	Temp.	S.	E.	k (obs.).	k (calc.).	$P \times 10^8$.
III.	Acetophenone ...	28°	24·5	12,100	0·01040	$1{\cdot}84 \times 10^4$	56·4
I.	Benzene	30	24	11,200	0·00219	$1{\cdot}2 \times 10^5$	1·9
II.	Benzene	38	24	8,088	0·00098	$2{\cdot}44 \times 10^7$	0·004
III.	Benzene	28	24	14,400	0·00030	$4{\cdot}6 \times 10^2$	64·8
III.	Toluene	28	21·6	15,100	0·00023	$1{\cdot}23 \times 10^2$	187·2
II.	Chloroform	38	21	10,760	0·00186	$3{\cdot}1 \times 10^5$	0·59
II.	Acetone	38	14	11,080	0·02690	$1{\cdot}6 \times 10^5$	16·8
III.	Acetone	28	14	13,600	0·00505	$1{\cdot}46 \times 10^3$	356·0
II.	Nitrobenzene ...	38	21·7	13,470	0·01350	$3{\cdot}4 \times 10^3$	400·0
III.	Nitrobenzene ...	28	21·7	13,300	0·01290	$2{\cdot}46 \times 10^3$	524
II.	Methyl alcohol	38	7·7	12,400	0·07480	$1{\cdot}73 \times 10^4$	432
II.	Ethyl alcohol ...	38	11·2	13,910	0·06260	$1{\cdot}62 \times 10^3$	3872
III.	Ethyl alcohol ...	28	11·2	15,100	0·00251	$1{\cdot}19 \times 10^2$	2100
II.	Butyl alcohol ...	38	22	14,060	0·05500	$1{\cdot}42 \times 10^3$	3888
II.	Benzyl alcohol	38	22	14,290	0·04400	$8{\cdot}9 \times 10^2$	4920

Although the three reactions considered are of the same type, these values of P show but little uniformity in their variation from solvent to solvent. However, they seem to be generally much smaller for non-polar than for polar solvents, and uniformly high for the alcohols. This may conceivably be due to the fact that the polar solvent molecule at the moment of collision forms a momentary complex with the potentially reactant molecules, which retains the energy in the system long enough for reaction to take place; the non-polar solvent, on the other hand, must be imagined to act only as a diluent to the energy in collisions between solute molecules reducing largely the number of effective collisions.

The Rôle of the Solvent.—It is well known that variation of the solvent has in most cases a very great effect on the velocity of a given reaction. In many cases, as, for example, in the mutarotation of sugars (Lowry and Faulkner, J., 1925, **127**, 2883), the solvent itself undoubtedly enters into the reaction as an intermediate reactant. In other cases, limiting factors, such as solubility and ionisation of one or more of the components, may affect the course of a reaction. Such cases must be separately considered on their

own merits. The formation of quaternary ammonium complexes, however, does in a general way appear to be linked up with the polar nature of the solvent (McCombie, Scarborough, and Smith, J., 1927, 802), and it has been suggested that in such cases the general action of the solvent is due to the electrical environment it provides for the reacting molecules (Norrish, J., 1923, **123**, 3006). A polar solvent may by close association create an induced polarity in the reacting molecules with the absorption of energy, and the consequent lowering of the critical increment of the reaction. We should therefore expect an increased velocity in the more polar solvents.

The facts now presented, however, make it clear that this is not the only general effect, and that we must also take account of the deactivating effect of the solvent as represented by the factor P, treated in the last section. It follows that, while a solvent may increase the velocity of a reaction by lowering the critical increment, yet there is always a reverse effect, due, as we believe, to the removal of energy from the potentially reactant molecules at the moment of collision by the molecules of the solvent.

Summary.

(1) *An attempt is made to apply the theory of kinetic activation to the investigation of reaction velocity in non-polar solution.*

(2) *The velocity of reaction between m- or p-nitrobenzyl chloride and trimethylamine in benzene solution has been determined for three temperatures.*

(3) The difference in the critical increments of the two reactions has been obtained by a comparison of their velocities and found to agree with that calculated from the temperature coefficients.

(4) The expression for the number of collisions between dissolved reactants has been considered, allowance being made for the more important effects of the solvent.

(5) The calculated velocity coefficients are in all cases greater than those determined experimentally.

(6) It is suggested in explanation that the probability factor connecting the number of potentially reactant with the number of reacting molecules is not unity, as in the case of gases, but is lowered by a deactivating effect of the solvent.

(7) This deactivating effect is considered to be connected with a removal of energy of activation by one or more of the solvent molecules at the moment of collision between the reactants.

(8) The rôle of the solvent is considered in the light of the probability factor in the reaction-velocity equation.

The thanks of one of us (F. F. P. S.) are due to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant which has made this work possible.

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XX.—*The Effect of the Constitution of a Chloroamine on its Hydrolysis Constant.*

By FREDERICK GEORGE SOPER and GILBERT FREEMAN SMITH.

THE methods available for the measurement of the hydrolysis constants of chloroamines have been described previously (J., 1924, **125**, 1899; 1925, **127**, 98). In the present investigation, 20% aqueous acetic acid (20 g. of acid in 100 c.c. of solution) was used as medium owing to its greater solvent power, which permitted determination of the hydrolysis constants over a much wider range of concentration than is possible in water. The primary and secondary hydrolysis constants of the standard chloroamine, *p*-toluenesulphondichloroamide, had to be redetermined in the new solvent, and the method was modified because the hydrolysis constant of chlorine therein was unknown.

The procedure adopted was to determine the ratio of the primary and secondary hydrolysis constants, K_1 and K_2, as before from the apparent solubility of the dichloroamide in solutions of the sulphonamide (*loc. cit.*, 1924, p. 1903); here, *a*, *b*, and *c*, are the concentrations in mols. per litre of unhydrolysed dichloroamide, monochloroamide, and free sulphonamide, respectively, and $K_1/K_2 = b^2/ac$. The hydrolysis constant of *N*-chloroacetanilide was then determined by distillation (*loc. cit.*, 1925, p. 101), allowance being made for the volatility of the unhydrolysed chloroamine. This knowledge, combined with determinations of the increased solubility (S) of the dichloroamide in acetanilide solutions, allowed of the calculation of K_1 and K_2 in the following way. If the equilibria existing in a saturated solution of *p*-toluenesulphondichloroamide in aqueous acetanilide are represented by

$$C_7H_7{\cdot}SO_2{\cdot}NCl_2 \rightleftharpoons C_7H_7{\cdot}SO_2{\cdot}NHCl + HOCl$$
$$\updownarrow$$
$$C_7H_7{\cdot}SO_2{\cdot}NH_2 + HOCl \Big\} \xrightarrow{C_6H_5{\cdot}NHAc} C_6H_5{\cdot}NClAc,$$

the thiosulphate titre, T_1, of the solution is given by

$$T_1 = 4[C_7H_7{\cdot}SO_2{\cdot}NCl_2] + 2[C_7H_7{\cdot}SO_2{\cdot}NHCl] + 2[C_6H_5{\cdot}NClAc] + 2[HOCl]$$

or, neglecting the last term, for reasons given in J., 1925, **127**, 100,

$$T_1 = 4a + 2b + 2x,$$

$$i.e., \ (T_1 - 4a)/2 = x + b = S \quad \ldots \quad (1)$$

where x is the concentration of the N-chloroacetanilide. The determination of K_1/K_2 from the solubility determination in the sulphonamide solution gives

$$b^2/ac = 13{\cdot}13, \text{ where } a = 0{\cdot}634 \times 10^{-3}\,M \quad . \ . \quad (2)$$

whilst the relation between the concentrations of sulphonamide and sulphonchloroamide requires that

$$x = b + 2c \quad \ldots \quad (3)$$

Hence from (1), (2), and (3)

$$b^2 + 8{\cdot}324 \times 10^{-3}\,b - 4{\cdot}162 \times 10^{-3}\,S = 0 \quad . \ . \quad (4)$$

This allows of the calculation of b, c, and x and also of [HClO] from the hydrolysis constant of N-chloroacetanilide,

$$[\mathrm{HClO}]\,(d - x)/x = 6{\cdot}70 \times 10^{-7} \quad . \ . \ . \ . \quad (5)$$

where d is the initial concentration of anilide, and hence of $K_1 = [\mathrm{HClO}]c/x$.

The values of K_1 and K_2 obtained in this way in 20% acetic acid are $5{\cdot}17 \times 10^{-7}$ and $3{\cdot}94 \times 10^{-8}$, respectively, whilst in water they were $8{\cdot}0 \times 10^{-7}$ and $4{\cdot}9 \times 10^{-8}$. From these values the hydrolysis constants of other chloroamines can be determined from the apparent solubility of the dichloroamide in solutions of the requisite anilide (*loc. cit.*, 1925, p. 99). [A correction should be made in equation (4) of that paper (p. 100) which should read $2[C_7H_7{\cdot}SO_2{\cdot}NH_2] = x - b$. The alteration has no appreciable effect on the constants given therein, since the sulphonamide concentration is always very slight.] The constants measured in water are in satisfactory agreement with the values now obtained in aqueous acetic acid over a much wider concentration range. The constant for N-chloro-p-toluidide is an exception and the relatively high value obtained in water has been traced to a further decomposition and oxidation which readily occurs in neutral aqueous solutions (see Chattaway and Orton, J., 1900, **77**, 792).

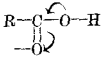
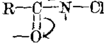
Effect of the Acyl Radical on the Hydrolysis of the Chloroamine.—The hydrolysis constants of the N-chloro-derivatives of four acylanilides are given in Table I, together with the ionisation constants, K_a, of the corresponding acids. The magnitude of the ionisation constant of the acid will be governed by the degree of polarisation of

TABLE I.

	$K_h \times 10^7$.	No. of determntns.		$K_a \times 10^4$.
N-Chloroformanilide	$1{\cdot}26 \pm 0{\cdot}04$	4	Formic acid	2·14
N-Chloroacetanilide	6·70 *	—	Acetic acid	0·186
N-Chloropropionanilide	$7{\cdot}5 \pm 0{\cdot}27$	3	Propionic acid	0·134
N-Chlorobutyranilide	$7{\cdot}0 \pm 0{\cdot}18$	4	Butyric acid	0·149—0·175

* The mean deviation from the mean has not been inserted for this case, which is taken as standard. It is estimated to be correct to within 10%.

the molecule as indicated in (I) (Allan, Oxford, Robinson, and Smith, J., 1926, 405; Ingold and Ingold, *ibid.*, p. 1311), being connected

(I.)   (II.)

with the degree of positiveness of the carbonyl carbon atom. If bivalent oxygen and tervalent nitrogen transmit the influence of the carbonyl carbon atom in the same way (II), we should expect that the ionisation of the chloroamine into positive chlorine, and therefore the hydrolysis constant of the chloroamine, would be increased in proportion to the increase in the ionisation constant of the acid. Actually an increase in the ionisation constant of the acid is attended by a decrease in the hydrolysis constant of the chloroamine. Increase in the positiveness of the carbonyl carbon thus causes a decrease of the hydrolysis of the chloroamine.

The effect of substituents in the benzene ring on the positivity of a nuclear carbon atom is indicated by the ionisation constants of the phenols, benzoic acids, and anilines. When the effect of substituents in the benzene ring on the hydrolysis of the chloroamine, $NClAc{\cdot}C_6H_5$, is studied, it is found that an increase in this positivity of the nuclear carbon atom attached to the NClAc group causes an *increase* in the hydrolysis of the chloroamine. The results obtained for the effects of the nitro-, methyl, and chlorine groups are given in Table II.

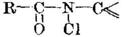
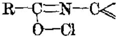
TABLE II.

Substituent.	$K_h \times 10^7$.	No. of determs.	$K_a \times 10^{10}$ for Ph·OH.	$K_a \times 10^5$ for $Ph{\cdot}CO_2H$.	$K_b \times 10^{10}$ for $Ph{\cdot}NH_2$.
H	6·7		1·1	6·0	5·0
o-NO_2	112 ± 3	4	750	620	0·00015—0·0004 *
m-NO_2	99 ± 4	6	100	34·5	0·04
p-NO_2	324 ± 22	4	960	40·0	0·01
o-CH_3	$1{\cdot}11 \pm 0{\cdot}02$	5	0·63	12·0	3·3
m-CH_3	$2{\cdot}61 \pm 0{\cdot}05$	5	0·98	5·1	6·0
p-CH_3	$3{\cdot}48 \pm 0{\cdot}12$	4	0·67	5·1	12—20
o-Cl	$6{\cdot}4 \pm 0{\cdot}30$	5	7·7	132	0·044 *
m-Cl	$23{\cdot}0 \pm 0{\cdot}5$	4		15·5	0·34
p-Cl	$16{\cdot}4 \pm 0{\cdot}3$	4	4·0	9·3	0·99

* Unpublished work in collaboration with Dr. G. Williams.

An explanation is thus required of the singular result that positiveness of the carbonyl carbon linked to nitrogen causes a decrease in the hydrolysis constant of the chloroamine, whilst positiveness of a nuclear carbon atom linked to nitrogen causes an increase in the hydrolysis constant of the chloroamine.

If one regards an acyl-chloroamine as represented either by the formula III, or by the possible formula IV (which is suggested by

(III.)   (IV.)

unpublished work on the kinetics of the formation of acylchloroamines), then increase in the positivity of either the carbonyl or the nuclear carbon atom should have the same effect on the hydrolysis constant of the chloroamine, in that either an increase or a decrease in this constant results.

A possible explanation of the observations may be that a chloroamine in solution consists of a tautomeric mixture of the (III) and (IV) forms. The effect of the positiveness of the carbonyl carbon is then to increase the ease with which positive chlorine can separate from a nitrogen atom (III), but to decrease the ease with which a negative OCl′ ion can separate from the carbonyl atom (IV). Since the induced effect of a group decreases rapidly with the distance, the positivity of the carbonyl carbon will affect the ionisation of its attached OCl′ ion to a greater extent than it will the ionisation of the positive chlorine attached to nitrogen, with the result that the hydrolysis is decreased. Conversely, increase in the positivity of the nuclear carbon atom will result in an increase of the hydrolysis owing to the proximity of the NCl group.

EXPERIMENTAL.

Preparation of 20% Aqueous Acetic Acid and its Stability to Chloroamines.—Commercial glacial acetic acid was purified by distillation from chromic anhydride (Orton and Bradfield, J., 1924, 125, 960). This acid was then diluted to approximately 20% with conductivity water and its strength adjusted after titration with $3N$-caustic soda, until it contained 20 g. of acetic acid per 100 c.c. of solution at 15°. When shielded from light, *p*-toluenedichlorosulphonamide, *N*-chloroacetanilide, and hypochlorous acid are fairly stable in this medium, as is seen from Table III.

Measurement of the Hydrolysis of N-*Chloroacetanilide by Distillation.*—The apparatus used has been previously described (*loc. cit.*). The distillate, consisting of hypochlorous acid and chloroamine, obtained from an $M/20$-N-chloroacetanilide solution in 20% acetic acid was $0{\cdot}002177M$ with respect to thiosulphate. In the presence

TABLE III.

Titre of 20 c.c. of solution (in c.c. of $N/500$-thiosulphate).

Time.	HOCl soln.	$C_6H_5{\cdot}NClAc$ soln.	$C_7H_7{\cdot}SO_2{\cdot}NCl_2$ soln.
0 hrs.	14·78 c.c.	17·12 c.c.	13·83 c.c.
12 ,,	14·55 ,,	17·07 ,,	13·70 ,,
21 ,,	14·25 ,,	17·00 ,,	13·59 ,,
34 ,,	13·50 ,,	16·68 ,,	13·59 ,,

of excess acetanilide, the distillate, now consisting of chloroamine only, was 0·001474*M*. The concentration of hypochlorous acid in the first distillate is therefore 0·000703*M*, corresponding to a concentration of 0·00183*M*-hypochlorous acid in the original solution. The latter deduction was made graphically from the results obtained on distillation of hypochlorous acid solution in 20% acetic acid (Table IV).

TABLE IV.

Distillation of hypochlorous acid solutions.

(*a*) C.c. of $N/500$-$Na_2S_2O_3$ required by 20 c.c. of solution	1·85	2·38	3·50	3·92	7·83	8·12
(*b*) C.c. of $N/500$-$Na_2S_2O_3$ required by 10 c.c. of distillate	3·55	4·43	7·05	7·29	13·10	13·24

From the concentration of free hypochlorous acid in the chloroamine solution, the hydrolysis constant can be calculated.

Solubility of p-*Toluenesulphondichloroamide.*—The solubility of *p*-toluenesulphondichloroamide in 20% acetic acid is 0·6343 × 10^{-3} mol. per litre. The solubilities in the various anilide solutions and in the solutions of the sulphonamide were measured in the manner already described (*loc. cit.*, 1925, p. 102). The results of two typical experiments are given in Table V.

TABLE V.

$d \times 10^3$.	$T_1 \times 10^3$.	$b \times 10^3$.	$x \times 10^3$.	$(d - x) \times 10^3$.	$[HOCl] \times 10^7$.	$K_h \times 10^7$.
			N-Chloro-*o*-chloroacetanilide.			
1	4·495	0·464	0·515	0·485	7·07	6·65
2	5·624	0·711	0·832	1·168	4·61	6·48
4	7·179	1·034	1·287	2·713	3·17	6·69
7	9·243	1·433	1·925	5·075	2·29	6·03
10	10·79	1·712	2·414	7·586	1·916	6·02
			N-Chloro-*o*-nitroacetanilide.			
3	3·667	0·274	0·291	2·709	12·0	111·4
5	3·975	0·346	0·373	4·627	9·48	117·6
7	4·305	0·422	0·463	6·537	7·77	109·8
10	4·665	0·502	0·562	9·438	6·54	109·8

Summary.

1. The hydrolysis constants of a number of acyl-chloroamines have been measured in 20% aqueous acetic acid.

2. Comparison of the hydrolysis constants of a series of chloroamines RR'NCl, in which R' was constant, with the ionisation constants of the fatty acids, ROH, shows that an increase in the latter is associated with a decrease in the hydrolysis constant of the chloroamine.

3. When the acyl group R is kept constant and the aryl radical R' is altered by the introduction of substituents, it is found that increase of the ionisation constant of the phenol, R'·OH, is attended by an *increase* in the hydrolysis constant of the chloroamine.

4. A possible explanation, based on the assumption that an acylchloroamine consists of a tautomeric mixture of the substances R·C(OCl):NR' and R·CO·NClR', is advanced.

In conclusion, we wish to express our appreciation of Professor K. J. P. Orton's continued interest in this work.

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BANGOR. [*Received, October 27th, 1927.*]

XXI.—*Researches on Residual Affinity and Co-ordination. Part XXX. Complex Ethylenethiocarbamido-salts of Univalent and Bivalent Metals.*

By GILBERT T. MORGAN and FRANCIS HEREWARD BURSTALL.

THAT associating units containing unoxidised sulphur conduce to the stability of complex salts of univalent copper and gold was illustrated by the behaviour of dimethyldithiolethylene towards cupric and auric chlorides when unstable additive products were formed which passed readily into stable complex cuprous and aurous derivatives (Morgan and Ledbury, *J.*, 1922, **121**, 2833).

Thiocarbamide (symbolised by tu in the following discussion) exerts a similar action on cupric salts, the products being, however, complicated by the circumstance that the base contains three associating foci, namely, two amino-radicals and a thiocarbonyl group. Owing to this dual character of thiocarbamide, its interaction with cupric nitrate leads, not only to the mononuclear cuprous salt, $[Cu,2tu]NO_3,H_2O$, but also to more complex polynuclear derivatives, $[Cu_2,5tu](NO_3)_2,1$ or $2H_2O$, $[Cu_3,7tu](NO_3)_3$ and $[Cu_5,11tu](NO_3)_5,8H_2O$, in which substances the amino-groups of thiocarbamide probably serve as bridging units between the metallic atoms of the complex kations (Rathke, *Ber.*, 1884, **17**, 297; Rosen-

heim and Loewenstamm, *Z. anorg. Chem.*, 1903, **34**, 62; Kohlschütter, *Ber.*, 1903, **36**, 1151; *Annalen*, 1906, **349**, 232).

We have now found that such complications are minimised by employing ethylenethiocarbamide, $\begin{matrix}CH_2\cdot NH\\ CH_2\cdot NH\end{matrix}\!\!>\!C{:}S$ (I; symbolised as etu), a cyclic compound in which the co-ordinating properties of the amino-groups of thiocarbamide are inhibited by involving the two nitrogen atoms in a stable five-membered ring.

1. *Ethylenethiocarbamido-cuprous Salts.*—By operating with ethylenethiocarbamide and cupric nitrate in hot aqueous solutions reduction to the cuprous condition occurs with elimination of sulphur; the colourless solution on concentration then furnishes *tetrakisethylenethiocarbamido-cuprous nitrate*, $[Cu,4etu]NO_3$, a remarkably stable salt neutral to litmus in aqueous solution. With a smaller proportion of ethylenethiocarbamide, a hydrated binuclear complex salt is formed, which loses three-fourths of its combined water at 110°, this change being reversed on exposing the partly dehydrated salt to the atmosphere: $[Cu_2,5etu,H_2O](NO_3)_2,3H_2O \rightleftarrows [Cu_2,5etu,H_2O](NO_3)_2$. The combining proportion of ethylenethiocarbamide to copper is affected by the chemical nature of the anion as shown by the compositions of the sulphate, acetate and halide salts.

When treated with aqueous alkalis, the foregoing cuprous salts give rise, not to cuprous oxide, but to a white, hydrous complex oxide which on drying has the composition $[Cu,etu]_2O$.

2. *Ethylenethiocarbamido-argentous Salts.*—Ethylenethiocarbamide combines with silver salts to form co-ordination compounds comparable with the preceding cuprous series. Two nitrates have been identified, *tetrakisethylenethiocarbamido-argentous nitrate*, $[Ag,4etu]NO_3$, and a binuclear *dinitrate*, $[Ag_2,3etu](NO_3)_2$. Silver chloride dissolves readily in aqueous ethylenethiocarbamide and the solution yields *trisethylenethiocarbamido-argentous chloride*, $[Ag,3etu]Cl$. The insoluble complex *oxide*, $[Ag,etu]_2O$, is precipitated in a hydrous form by the action of alkalis on the preceding salts. It is noteworthy that these thiocarbamido-argentous salts are not photosensitive on exposure to ordinary daylight.

3. *Ethylenethiocarbamido-aurous Salts.*—With ethylenethiocarbamide, an aqueous solution of auric chloride yields at first an orange caseous precipitate which on boiling speedily dissolves with loss of colour; the concentrated solution yields *bisethylenethiocarbamido-aurous chloride*, $[Au,2etu]Cl,H_2O$. Addition of nitric acid to the colourless solution gives rise to a complex *nitrate*, $[Au,2etu]NO_3$, which differs from the thiocarbamido-derivative, $[Au,2tu]NO_3,H_2O$, in being anhydrous (compare Reynolds, J., 1869, **22**, 1). The com-

plex *hydrated bromide*, $[Au,2etu]Br,H_2O$, is readily soluble, whereas the *iodide*, [Au,etu]I, dissolves only sparingly and the white, insoluble, amorphous *oxide*, $[Au,etu]_2O$, corresponds with the complex oxides of the copper and silver series (pp. 149, 151).

4. *Ethylenethiocarbamido Salts of Bivalent Metals.*—Attempts to combine zinc nitrate with ethylenethiocarbamide in aqueous or alcoholic solution were fruitless, although combination occurred with cadmium and mercury salts. The complex *cadmium nitrate*, $[Cd,4etu](NO_3)_2$ is readily soluble in water to a neutral solution.

Trisethylenethiocarbamido-mercuric nitrate, $[Hg,3etu](NO_3)_2$, which is neutral to litmus in aqueous solution, may be prepared by interaction of ethylenethiocarbamide with either mercurous or mercuric nitrate, its formation in the former case being accompanied by elimination of mercury. The sparingly soluble complex chloride, $3HgCl_2,2etu$, had already been described by Hofmann (*Ber.*, 1873, **6**, 598).

Lead salts do not lend themselves readily to combinations with ethylenethiocarbamide, but the complex dichloride, $PbCl_2,etu$, has been obtained as a sparingly soluble product.

Palladous chloride and the thio-base combine to form the orange *tetrakisethylenethiocarbamido-palladous chloride*, $[Pd,4etu]Cl_2$, a slightly modified procedure leading to the dark brown complex *nitrate*, $[Pd,4etu](NO_3)_2$. Both salts are very sparingly soluble in cold water.

Electronic Structure of Ethylenethiocarbamido Metallic Nitrates.

Owing to its cyclic structure, ethylenethiocarbamide probably functions as a single associating unit in the salts under discussion and accordingly each molecule of base contributes to the co-ordination complex two electrons derived from its sulphur atom.

In the compounds examined, the limiting type is reached by a fourfold co-ordination between metal and thio-base as shown by the following series of nitrates: $[Cu,4etu]NO_3$, $[Ag,4etu]NO_3$, $[Cd,4etu](NO_3)_2$, $[Pd,4etu](NO_3)_2$. The cuprous ion is 8 electrons short of the number required for the rubidium ion, but by becoming co-ordinated with 4 molecular proportions of cyclic thio-base it acquires these additional electrons.

$$\begin{array}{lll} Cu^{I} + 4etu = [Cu,4etu]^{I} & & Rb^{I} \\ 2,8,18 \quad 8 \qquad 2,8,18,8 & & 2,8,18,8. \end{array}$$

Similar relationships may be traced in the complex nitrates derived from silver and cadmium ions, the silver and cadmium com-

plexes being electronically equivalent to cæsium and barium ions, respectively.

$Ag^{I} + 4etu = [Ag,4etu]^{I}$	Cs^{I}
2,8,18,18 8 2,8,18,18,8	2,8,18,18,8
$Cd^{II} + 4etu = [Cd,4etu]^{II}$	Ba^{II}
2,8,18,18 8 2,8,18,18,8	2,8,18,18,8.

Experimental support for these analogies is afforded by the observation that these soluble complex nitrates behave like nitrates of the metals of the alkalis and alkaline earths in giving rise to neutral solutions. Moreover, a further similarity is discerned on determining the electrical conductivities of these aqueous solutions. The following table gives the molecular conductivities (in reciprocal ohms) of solutions containing one g.-mol. of complex nitrate in *v* litres of water at 25°:

v	32	64	128	256	512	1024
$[Cu,4etu]NO_3$	87	92·5	96	98·3	103	121
$[Ag,4etu]NO_3$	81·4	89·2	94·1	97·8	97·2	—
$[Cd,4etu](NO_3)_2$	187·2	203·5	220·4	231·3	237·6	238
$[Au,2etu]NO_3$	96·7	104·4	108·2	110·4	109·7	111·2
$[Hg,3etu](NO_3)_2$	142·7	161·0	170·2	178·0	181	181·5

These values for electrical conductivity show that in aqueous solutions the co-ordination complexes $[Metal,4etu]^{I \text{ or } II}$ play the part of compound *alkali radicals*.

This electronic analogy between the ethylenethiocarbamido-complexes and the metallic ions of the alkalis and alkaline earths is not, however, fulfilled so completely in the cases of the complex aurous and mercuric nitrates, the electrical conductivities of which are inserted in the foregoing table for the purposes of comparison. The ethylenethiocarbamido-aurous complex is still 4 electrons short of the number required for the hypothetical eka-cæsium and the mercuric complex is 2 electrons short of the number required for the radium ion as shown below:

$Au^{I} + 2etu$	=	$[Au,2etu]^{I}$	ekaCs^{I}
2,8,18,32,18, 4		2,8,18,32,18,4	2,8,18,32,18,8
$Hg^{II} + 3etu$	=	$[Hg,3etu]^{II}$	Ra^{II}
2,8,18,32,18 6		2,8,18,32,18,6	2,8,18,32,18,8

Nevertheless, the two complex aurous and mercuric nitrates dissolve in water to neutral solutions which have high electrical conductivities.

The palladous ion is 10 electrons short of the number required for the cæsium ion and in both complex salts (nitrate and chloride) the metal is associated with 4 molecular proportions of ethylene-

thiocarbamide, so that the complex is still 2 electrons short of the limiting number. The complex chloride and nitrate are, however, of very sparing solubility, this fact suggesting a considerable degree of association, which persists in the presence of water. But in spite of low solubility, the electrical conductivity of the nitrate has been determined with a dilution of 1 g.-mol. in 1024 litres and found to be 156·6 reciprocal ohms at 25°. This result indicates that the dissolved nitrate is an electrolyte having the structural formula $[Pd,4etu](NO_3)_2$. Moreover, cold saturated solutions of the nitrate and chloride, although very dilute, give ionic reactions with "nitron" acetate and silver nitrate respectively.

EXPERIMENTAL.

Ethylenethiocarbamide, melting at 194°, was prepared according to Hofmann's method (*Ber.*, 1872, **5**, 240).

1. *Ethylenethiocarbamido-cuprous Salts.*

Tetrakisethylenethiocarbamido-cuprous Nitrate, $[Cu,4etu]NO_3$.—On mixing warm aqueous solutions of 5·0 g. of ethylenethiocarbamide and 2·5 g. of cupric nitrate, a green colour was developed which rapidly faded; and the colourless liquid became opaque owing to the separation of sulphur. The filtrate on concentration and cooling deposited long, colourless, prismatic crystals, which were purified by recrystallisation from warm water (Found: C, 27·0; H, 4·8; N, 23·3; S, 24·3; Cu, 11·9. $C_{12}H_{24}O_3N_9S_4Cu$ requires C, 27·0; H, 4·5; N, 23·6; S, 24·0; Cu, 11·9%). This complex nitrate, which melted to a colourless liquid at 140—141°, was readily soluble in water to neutral and stable solutions, but insoluble in the common organic media. An aqueous solution gave a brown, colloidal suspension with hydrogen sulphide or yellow ammonium sulphide, cuprous sulphide being precipitated on warming. Caustic soda and sodium carbonate in the cold produced flocculent precipitates changing to a white, granular oxide on boiling. Ammonium hydroxide caused the separation of a white solid in concentrated but not in dilute solutions of the complex nitrate; a blue colour was slowly developed in both cases. Hydrochloric acid gave an immediate precipitate, soluble on warming and crystallising on cooling to a felted mass of white needles. Dilute nitric acid slowly produced a white crystalline deposit. Disodium hydrogen phosphate had no action in the cold, but on warming a white precipitate was formed which redissolved on cooling. Both potassium ferrocyanide and ferricyanide gave amorphous deposits, the former, a white solid decomposed on boiling and the latter, a reddish-brown solid unaffected by warming. Sodium cyanide and potassium iodide

precipitated white solids, the former soluble in excess of reagent but not on boiling, whereas the latter dissolved on heating but was unaffected by excess of iodide. These chemical reactions and the insolubility in organic media are properties also characteristic of the following cuprous salts.

Monoaquopentaethylenethiocarbamido-dicuprous Nitrate Trihydrate, $[Cu_2,5etu,H_2O](NO_3)_2,3H_2O$.—On adding aqueous cupric nitrate (2·5 g.) to a warm solution of ethylenethiocarbamide (3·0 g.), a colourless liquid was obtained with deposition of sulphur. After evaporation and cooling, large, white, six-sided, prismatic crystals separated which were recrystallised and air-dried (Found: C, 21·7, 21·6; H, 4·8, 4·5; N, 20·2; S, 18·8; Cu, 15·1. $C_{15}H_{38}O_{10}N_{12}S_5Cu_2$ requires C, 21·6; H, 4·6; N, 20·2; S, 19·2; Cu, 15·25%).

This complex nitrate melted to a colourless liquid at 145—146°. Its freshly prepared aqueous solution was colourless and neutral to litmus, but soon oxidised when exposed to air. When this hydrated salt was left over sulphuric acid, it lost three molecules of its combined water, leaving a white residue of *monoaquopentaethylenethiocarbamido-dicuprous nitrate,* $[Cu_2,5etu,H_2O](NO_3)_2$ (Found: C, 22·6; H, 4·3; N, 22·1; S, 19·8; Cu, 16·3. $C_{15}H_{32}O_7N_{12}S_5Cu_2$ requires C, 23·1; H, 4·1; N, 21·6; S, 20·6; Cu, 16·3%. Found: loss of water, 6·2. Calc. for $3H_2O$, 6·3%). This dehydrated salt was exceedingly hygroscopic and was also easily oxidised, becoming green on keeping.

Trisethylenethiocarbamido-cuprous Sulphate, $[Cu,3etu]_2SO_4$.—An aqueous solution of cupric sulphate (2·5 g.) and ethylenethiocarbamide (5·0 g.) was heated until colourless; the sparingly soluble sulphate separated in almost quantitative yield on cooling, and was recrystallised from hot water containing ethylenethiocarbamide. Colourless, three-sided prisms separated which were washed with water and dried over sulphuric acid (Found: C, 25·9; H, 4·5; N, 20·5; S, 27·5; Cu, 15·2. $C_{18}H_{36}O_4N_{12}S_7Cu_2$ requires C, 25·8; H, 4·3; N, 20·1; S, 26·8; Cu, 15·2%). This complex sulphate was quite stable in air, but when heated it blackened at 240° and melted with decomposition at 251°. Barium chloride gave an immediate precipitate with aqueous solutions of the complex sulphate, showing that this salt was ionised in aqueous media.

Trisethylenethiocarbamido-cuprous Acetate, $[Cu,3etu]C_2H_3O_2$, separated, when a warm decolorised solution of its generators was cooled, in colourless, elongated plates and was recrystallised from water containing ethylenethiocarbamide (Found: N, 19·5; S, 22·3; Cu, 14·9, 15·0. $C_{11}H_{21}O_2N_6S_3Cu$ requires N, 19·6; S, 22·4; Cu, 14·8%). This complex acetate was stable in air, but on heating it decomposed with blackening at 250—255°. It was fairly soluble

in warm water, the solution being neutral to litmus and stable on boiling.

Bisethylenethiocarbamido-cuprous Chloride [Cu,2etu]Cl.—Freshly prepared cuprous chloride (1·0 g.) was dissolved in a hot aqueous solution of ethylenethiocarbamide (3·0 g.), and the filtrate evaporated to 70 c.c.; transparent, rhombic crystals were then deposited (Found: C, 23·5; H, 4·2; N, 18·3; S, 21·5; Cl, 11·3; Cu, 20·6. $C_6H_{12}N_4ClS_2Cu$ requires C, 23·7; H, 4·0; N, 18·5; S, 21·15; Cl, 11·7; Cu, 21·0%). The complex chloride melted to a colourless liquid at 166—167°. Although soluble in aqueous ethylenethiocarbamide, this salt decomposed in pure water; the crystals became opaque and a large part of the complex chloride remained undissolved, even on boiling.

The complex *bromide*, [Cu,2etu]Br, crystallised in small clumps of transparent, glistening rhombohedra (m. p. 162—163°), which were recrystallised from aqueous ethylenethiocarbamide (Found: C, 20·4; H, 3·9; N, 16·6; S, 17·85; Br, 22·8; Cu, 18·55. $C_6H_{12}N_4BrS_2Cu$ requires C, 20·7; H, 3·5; N, 16·5; S, 18·4; Br, 23·0; Cu, 18·3%).

The complex *iodide*, [Cu,2etu]I, after recrystallisation from aqueous ethylenethiocarbamide, was obtained as a white, crystalline powder, m. p. 160—161° (Found: C, 18·6; H, 3·4; N, 14·0; S, 15·8; I, 31·8; Cu, 15·75. $C_6H_{12}N_4IS_2Cu$ requires C, 18·2; H, 3·1; N, 14·2; S, 16·2; I, 32·15; Cu, 16·1%).

Ethylenethiocarbamido-cuprous Oxide, $[Cu,etu]_2O$.—The flocculent white precipitate produced on adding excess of aqueous sodium hydroxide to a cold solution of tetrakisethylenethiocarbamido-cuprous nitrate was rendered granular by heating the turbid mixture to boiling. The segregated deposit was washed with hot water until free from alkali salts and dried over sulphuric acid (Found: C, 21·5, 21·2; H, 3·6, 3·5; N, 16·9; S, 18·2; Cu, 37·0. $C_6H_{12}ON_4S_2Cu_2$ requires C, 20·7; H, 3·5; N, 16·5; S, 18·5; Cu, 36·6%). This complex oxide, which darkened at 180° and decomposed without melting at 200°, was a white powder very slowly becoming tinged with blue on exposure to air. It dissolved in warm dilute hydrochloric and sulphuric acids to solutions which deposited crystalline complex cuprous salts on cooling. Dilute nitric acid and sodium cyanide both had a solvent action, but the oxide was insoluble in ammonia although slowly oxidised in contact with this reagent.

Pentathiocarbamido-dicuprous Cyanate Hydrate,

$[Cu_2,5tu](CNO)_2,H_2O$.

—When excess of a concentrated aqueous solution of potassium cyanate was added to aqueous cupric sulphate saturated with sulphur dioxide, a white crystalline double salt was deposited approximat-

ing in composition to the formula $Cu_2K(CNO)_3$. This compoun when triturated with a cold concentrated solution of thiocarbamide dissolved to a solution from which colourless tufts of acicula crystals separated (Found: C, 13·7; H, 3·5; N, 27·4; S, 26·85 Cu, 20·8. $C_7H_{22}O_3N_{12}S_5Cu_2$ requires C, 13·8; H, 3·6; N, 27·6 S, 26·3; Cu, 20·85%). The complex cyanate, which decompose at 135°, was soluble in water but insoluble in organic solvents. It aqueous solution slowly decomposed in the cold and very rapidl on warming, giving cuprous sulphide. Cold aqueous caustic soda solution produced an immediate black precipitate.

2. *Ethylenethiocarbamido-argentous Salts.*

Tetrakisethylenethiocarbamido-argentous Nitrate, $[Ag,4etu]NO_3$.—A warm aqueous solution of 1·7 g. of silver nitrate and 4·0 g. c ethylenethiocarbamide deposited, on cooling, radiating clusters c colourless acicular prisms, which were recrystallised from a smal amount of water (Found: C, 24·6, 24·75; H, 4·6, 5·1; N, 22·2 S, 22·1; Ag, 18·6. $C_{12}H_{24}O_3N_9S_4Ag$ requires C, 24·9; H, 4·2 N, 21·8; S, 22·2; Ag, 18·7%). This complex nitrate, which melte to a colourless liquid at 96—97°, was readily soluble in water an slightly soluble in alcohol, but insoluble in other organic media With potassium iodide, the nitrate gave a white precipitate, decom posed on boiling and leaving a residue of silver iodide. Thes chemical reactions are also characteristic of the series of silver salts except that the following compounds are insoluble in alcohol an other organic media.

Trisethylenethiocarbamido-diargentous Nitrate, $[Ag_2,3etu](NO_3)_2$.—When an aqueous solution of silver nitrate (1·7 g.) was added to a solution of ethylenethiocarbamide (2·0 g.) in 400 c.c. of water, an amorphous, white precipitate was deposited which readily redis solved on heating. On slow cooling, the liquid became filled with a mass of felted, colourless, silky needles which, being only sparingly soluble, required a large volume of hot water for recrystallisation (Found: C, 17·15, 17·2; H, 3·35, 3·1; N, 17·8; S, 15·2; Ag, 33·1 $C_9H_{18}O_6N_8S_3Ag_2$ requires C, 16·7; H, 2·8; N, 17·3; S, 14·9 Ag, 33·4%). The salt blackened at 200° and decomposed with explosive violence at 224°.

Trisethylenethiocarbamido-diargentous persulphate, $[Ag_2,3etu]S_2O_8$, was obtained as a colourless crystalline precipitate when a cold concentrated solution of potassium persulphate was added to a cold aqueous solution of tetrakisethylenethiocarbamido-argentous nitrate (Found: C, 14·6; H, 2·8; N, 11·9; S, 23·0; Ag, 29·9. $C_9H_{18}O_8N_6S_5Ag_2$ requires C, 15·1; H, 2·55; N, 11·8; S, 22·4; Ag, 30·2%). The complex persulphate was quite stable in air; it

darkened at 160° and melted with decomposition at 205°. The sparingly soluble complex salt was slowly decomposed by warm water. It liberated iodine from acidified potassium iodide.

Trisethylenethiocarbamido-argentous Chloride, [Ag,3etu]Cl.—A freshly prepared sample of silver chloride (1·4 g.) was dissolved in an aqueous solution of ethylenethiocarbamide (3·0 g.). The hot solution, when filtered, evaporated and cooled, deposited a mass of small white needles. This readily soluble complex chloride was recrystallised from hot water (Found: C, 24·4; H, 4·2; N, 19·0; S, 21·8; Cl, 7·7; Ag, 23·5. $C_9H_{18}N_6ClS_3Ag$ requires C, 24·0; H, 4·0; N, 18·7; S, 21·4; Cl, 7·9; Ag, 24·0%). This complex silver salt was very stable and quite unaffected by light. It melted to a colourless liquid at 167—168°.

Bisethylenethiocarbamido-argentous bromide, [Ag,2etu]Br, was prepared in a similar manner to the foregoing chloride, but it was found necessary to add ethylenethiocarbamide in order to obtain complete solution during recrystallisation (Found: C, 18·7; H, 3·5; N, 14·0; S, 16·0; Br, 20·3; Ag, 27·4. $C_6H_{12}N_4BrS_2Ag$ requires C, 18·4; H, 3·1; N, 14·3; S, 16·4; Br, 20·4; Ag, 27·5%). The complex bromide, obtained in short, prismatic crystals, melted at 152° and was only sparingly soluble in water even on boiling. It resembled the corresponding cuprous bromide complex in the loss of its crystalline appearance in these circumstances (p. 149).

Ethylenethiocarbamido-argentous Iodide, [Ag,etu]I.—Owing to the insolubility of silver iodide in aqueous ethylenethiocarbamide, a modified method had to be used for the isolation of a complex silver iodide derivative. Potassium iodide was added in slight excess to an aqueous solution of tetraethylenethiocarbamido-argentous nitrate. The microcrystalline precipitate was filtered off, washed with a little cold water, and dried over sulphuric acid (Found: *N, 7·3; S, 8·8; I, 38·8; Ag, 33·7.* $C_3H_6N_2ISAg$ *requires N, 8·3;* S, 9·5; I, 37·7; Ag, 32·0%). The poor analytical results obtained for this complex iodide were due to dissociation during washing. This sparingly soluble salt melted at 162° to a yellow liquid.

Ethylenethiocarbamido-argentous Oxide, $[Ag,etu]_2O$.—Pure aqueous sodium hydroxide was added in slight excess to a boiling solution of tetrakisethylenethiocarbamido-argentous nitrate. The white granular precipitate was washed free of alkali salts with hot water and dried in a vacuum over sulphuric acid (Found: C, 16·7; H, 2·9; N, 12·6; S, 14·5; Ag, 50·1. $C_6H_{12}ON_4S_2Ag_2$ requires C, 16·5; H, 2·8; N, 12·85; S, 14·7; Ag, 49·5%). This complex oxide slowly decomposed on keeping, its surface becoming brown and finally black; it darkened at 120° and decomposed at 170°. It dissolved readily in warm dilute hydrochloric and sulphuric acids, the solutions

giving crystalline salts on cooling. Dilute nitric acid and sodium cyanide also exercised a solvent action in hot solutions.

3. *Ethylenethiocarbamido-aurous Salts.*

Bisethylenethiocarbamido-aurous Nitrate, $[Au,2etu]NO_3$.—An aqueous solution of auric chloride, $HAuCl_4,3H_2O$ (2·0 g.) was added to one of ethylenethiocarbamide (2·0 g.). The orange precipitate at first formed, immediately redissolved on warming and the solution became colourless. Dilute nitric acid was then added in slight excess and white feathery crystals separated on cooling (Found: C, 15·85; H, 2·75; N, 14·9; S, 14·2; Au, 42·3. $C_6H_{12}O_3N_5S_2Au$ requires C, 15·5; H, 2·6; N, 15·1; S, 13·8; Au, 42·55%). The complex nitrate melted with decomposition at 173°. It was soluble in water and in warm alcohol, giving stable and neutral solutions in both solvents, but insoluble in ether, acetone, benzene, and chloroform. Caustic soda, sodium carbonate, and ammonium hydroxide all gave white precipitates with a solution of this complex nitrate. Sodium cyanide and potassium iodide produced white solids, the former soluble in excess of reagent, whereas the latter decomposed on boiling. Hydrogen sulphide formed a yellow, colloidal suspension of aurous sulphide, precipitated by heat. Potassium ferrocyanide gave a white salt which changed on heating to yellow, green, and finally blue. The complex nitrate was not reduced to colloidal gold by formaldehyde.

Bisdiethylenethiocarbamido-aurous Chloride Hydrate,

$[Au,2etu]Cl,H_2O$.

—On warming an aqueous solution containing equal parts of auric chloride, $HAuCl_4,3H_2O$, and ethylenethiocarbamide, the liquid became decolorised and turbid. The concentrated filtrate deposited pearly plates, which were recrystallised from water and dried over sulphuric acid (Found: C, 16·1; H, 3·5; N, 12·7; S, 14·55; Cl, 7·6; Au, 42·9, 43·0. $C_6H_{14}ON_4ClS_2Au$ requires C, 15·8; H, 3·1; N, 12·3; S, 14·1; Cl, 7·8; Au, 43·3%). This complex chloride became yellow at 210° and melted with decomposition at 242°. When the salt was maintained at 110°, water was eliminated, leaving a residue of anhydrous *bisethylenethiocarbamido-aurous chloride*, [Au,2etu]C (Found: loss, 4·1. Calc. for $1H_2O$, 4·0%). The chloride was easil soluble in water and alcohol but insoluble in other organic media.

Bisethylenethiocarbamido-aurous Bromide Hydrate,

$[Au,2etu]Br,H_2O$.

—The white precipitate produced by adding excess of sodium hydr oxide to an aqueous solution of the preceding complex chloride wa dissolved in warm, dilute hydrobromic acid containing ethylenethio carbamide. The cooled solution yielded colourless needles of the

complex bromide, which were recrystallised from warm water and dried over calcium chloride (Found: Au, 39·75. $C_6H_{14}ON_4BrS_2Au$ requires Au, 39·5%). This complex bromide, which was readily soluble in alcohol, melted in its water of crystallisation at 100°, then resolidified and melted again to a colourless liquid at 191°. When left over sulphuric acid, it became dehydrated into *bisethylenethiocarbamido-aurous bromide*, [Au,2etu]Br, which reverted to the monohydrate on exposure to the atmosphere (Found: C, 15·3; H, 2·9; N, 11·9; Br, 16·3; Au, 40·5. $C_6H_{12}N_4BrS_2Au$ requires C, 15·0; H, 2·5; N, 11·6; Br, 16·6; Au, 41·0%. Found: loss on drying, 3·3. Required for $1H_2O$, 3·6 %).

Ethylenethiocarbamido-aurous iodide, [Au,etu]I, separated as a sparingly soluble, white powder, melting with decomposition at 225°, on addition of potassium iodide to an aqueous solution of the complex chloride (Found: C, 8·7; H, 1·7; N, 6·8; I, 30·1; Au, 46·0. $C_3H_6N_2ISAu$ requires C, 8·45; H, 1·4; N, 6·6; I, 29·8; Au, 46·4%).

Ethylenethiocarbamido-aurous Oxide, $[Au,etu]_2O$.—Pure caustic soda added in slight excess to an aqueous solution of aquobisethylenethiocarbamido-aurous chloride produced a white, flocculent precipitate, which was granulated by boiling and washed thoroughly with hot water until free from alkali salts (Found: C, 11·45; H, 2·1; N, 9·3; S, 10·5; Au, 64·8. $C_6H_{12}ON_4S_2Au_2$ requires C, 11·7; H, 2·0; N, 9·1; S, 10·4; Au, 64·2%). This complex aurous oxide blackened at 200° and became blue on exposure. It differed from the corresponding cuprous and silver oxides in being decomposed by dilute mineral acids. Although unaffected by dilute alkali, it was readily soluble in warm sodium cyanide solution.

Bisthiocarbamido-aurous Nitrate Hydrate, $[Au,2tu]NO_3,H_2O$.—Dilute nitric acid added to a solution of auric chloride decolorised by thiocarbamide produced an amorphous, white precipitate; this dissolved in warm water and separated again in an amorphous condition, but gradually redissolved and was replaced by lustrous, colourless crystals, which were air-dried (Found: C, 5·4; H, 2·5; N, 16·1; S, 15·4; Au, 45·8. $C_2H_{10}O_4N_5S_2Au$ requires C, 5·6; H, 2·3; N, 16·3; S, 14·9; Au, 45·9%). This complex nitrate, although stable in air, was slowly decomposed by light; it decomposed at 155°. It was readily soluble in alcohol but not in other organic media. The aqueous solution decomposed slightly on boiling. Caustic soda gave a yellow precipitate in the cold but, on warming, this rapidly darkened. When desiccated over sulphuric acid, this complex nitrate lost water, leaving an opaque residue of *bisthiocarbamido-aurous nitrate*, $[Au,2tu]NO_3$ (Found: C, 5·75; H, 2·1; Au, 48·0. $C_2H_8O_3N_5S_2Au$ requires C, 5·8; H, 2·0; Au, 47·9%. Found: loss, 4·5. Calc. for $1H_2O$, 4·2%).

4. *Ethylenethiocarbamido Salts of Bivalent Metals.*

Tetrakisethylenethiocarbamido-cadmium nitrate, $[Cd,4etu](NO_3)_2$ separated in large, tabular crystals on concentrating an aqueous solution of cadmium nitrate (3·0 g.) and ethylenethiocarbamide (4·0 g.) and was recrystallised from water until colourless (Found: C, 22·9; H, 4·1; N, 21·5; S, 19·8; Cd, 17·2. $C_{12}H_{24}O_6N_{10}S_4Cd$ requires C, 22·3; H, 3·75; N, 21·7; S, 19·9; Cd, 17·4%). The complex nitrate melted at 178° and was quite stable in air. It was insoluble in organic media and its aqueous solution gave gelatinous precipitates with caustic soda and sodium carbonate, and cadmium sulphide with hydrogen and ammonium sulphides.

Bisethylenethiocarbamido-cadmium chloride, $[Cd,2etu]Cl_2$, crystallised from a large volume of water in sparingly soluble, colourless, prismatic needles (Found: C, 18·8; H, 3·55; N, 15·0; S, 16·4; Cl, 17·9; Cd, 28·6. $C_6H_{12}N_4Cl_2S_2Cd$ requires C, 18·6; H, 3·1; N, 14·5; S, 16·5; Cl, 18·3; Cd, 29·0%). This complex chloride, which melted to a yellow liquid at 220°, was neutral to litmus in aqueous solution.

The complex *bromide,* $[Cd,2etu]Br_2$, crystallised in flat, colourless plates (Found: C, 15·1; H, 2·5; N, 11·5; S, 13·2; Br, 33·6; Cd, 23·75. $C_6H_{12}N_4Br_2S_2Cd$ requires C, 15·1; H, 2·5; N, 11·8; S, 13·5; Br, 33·5; Cd, 23·55%). This salt, which melted to a yellow liquid at 208°, was more soluble in water than the corresponding chloride.

The complex *iodide,* $[Cd,2etu]I_2$, crystallised from aqueous solution in white opaque needles (Found: C, 13·0; H, 2·2; N, 10·0; S, 11·5; I, 44·2; Cd, 19·5. $C_6H_{12}N_4I_2S_2Cd$ requires C, 12·6; H, 2·1; N, 9·8; S, 11·2; I, 44·5; Cd, 19·7%). This salt, the most soluble of the three halides, melted to a colourless liquid at 165°.

Ethylenethiocarbamido-plumbous chloride, $[Pb,etu]Cl_2$, a sparingly soluble compound, crystallised in colourless plates when a hot solution of lead chloride in aqueous ethylenethiocarbamide was cooled. It melted to a yellow liquid at 183° (Found: C, 9·6; H, 1·75; N, 7·45; S, 8·7; Cl, 18·5; Pb, 54·6. $C_3H_6N_2Cl_2SPb$ requires C, 9·5; H, 1·6; N, 7·4; S, 8·4; Cl, 18·7; Pb, 54·5%).

Trisethylenethiocarbamido-mercuric nitrate, $[Hg,3etu](NO_3)_2$, separated in colourless rhombic plates on concentrating an aqueous solution containing two parts of mercuric nitrate and three of ethylenethiocarbamide; it decomposed at 196° (Found: N, 17·55; S, 14·9; Hg, 32·0. $C_9H_{18}O_6N_8S_3Hg$ requires N, 17·8; S, 15·25; Hg, 31·8%). Aqueous caustic soda produced a flocculent white precipitate, but the nitrate was unaffected by dilute mineral acids.

Tetrakisethylenethiocarbamido-palladous Chloride, $[Pd,4etu]Cl_2$.—On cooling a boiling aqueous solution of ethylenethiocarbamide to which a third of its weight of palladium chloride had been added,

the complex chloride separated in lustrous orange spangles, which were recrystallised from a large volume of hot water (Found: C, 24·8; H, 4·3; N, 19·75; S, 22·2; Cl, 11·9; Pd, 18·6. $C_{12}H_{24}N_8Cl_2S_4Pd$ requires C, 24·6; H, 4·1; N, 19·1; S, 21·9; Cl, 12·1; Pd, 18·2%). This complex chloride blackened at 210° and melted at 270°. It was insoluble in organic media, but in aqueous solution, caustic and carbonated alkalis gave yellow, amorphous precipitates; potassium iodide developed a deep red coloration, and palladium sulphide was precipitated in warm solutions by hydrogen or ammonium sulphide. A cold saturated solution of the chloride containing less than 0·01% of dissolved substance gave slowly an appreciable precipitate with silver nitrate. In warm concentrated solutions precipitation was rapid and copious.

Tetrakisethylenethiocarbamido-palladous Nitrate, $[Pd,4etu](NO_3)_2$.—Aqueous palladium chloride (1·7 g.) was added to ethylenethiocarbamide (2·0 g.) dissolved in dilute sodium hydroxide solution and the resulting brown precipitate was dissolved in 500 c.c. of water containing 15 c.c. of 2*N*-nitric acid and 4 g. of ethylenethiocarbamide. The complex nitrate separated in almost black nodules on cooling and was recrystallised from a large volume of hot water (Found: N, 22·0; Pd, 16·7. $C_{12}H_{24}O_6N_{10}S_4Pd$ requires N, 21·9; Pd, 16·7%). The nitrate melted with decomposition at 235°; it was only sparingly soluble in alcohol and insoluble in other organic solvents. With aqueous "nitron" acetate a cold saturated solution of the complex nitrate containing 0·012% of dissolved substance slowly gave a crystalline precipitate of "nitron" nitrate, precipitation being immediate and copious in hot, concentrated solutions.

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XXII.—*Observations on the Chlorination Products of ββ′-Dichlorodiethyl Sulphide.*

By Stanley Augustus Mumford and John William Cole Phillips.

In the course of other investigations, it was necessary to prepare the compounds described by Mann and Pope (J., 1922, **121**, 594) as αββ′-trichloro-, αβββ′-tetrachloro-, and ααβββ′-hexachloro-diethyl sulphides, obtained by the chlorination of ββ′-dichlorodiethyl sulphide $(CH_2Cl·CH_2)_2S$.

All three compounds as formulated above contain an α-chlorine atom. Now it is a well-known fact that the α-halogen atoms in α-halogen-substituted alkyl ethers are only very loosely attached,

and extension of this general statement to include α-halogenated alkyl sulphides would appear to be justifiable from numerous observations recorded in the literature. For example, according to Mann and Pope (J., 1923, **123**, 1172), αα′-dichlorodiethyl sulphide $(CH_3{\cdot}CHCl)_2S$, is considerably less stable than the ββ′-isomeride. Peters and Walker (*Biochem. J.*, 1923, **17**, 272) have found that αα′-dichlorodimethyl sulphide is very readily hydrolysed, and Bales and Nickelson (J., 1922, **121**, 2137; 1923, **123**, 2486) have shown that, in general, α-halogenated ethyl sulphides are unstable and decompose on keeping.

Of the tri-, tetra-, and hexa-chloro-derivatives described by Mann and Pope, the last is considerably hydrolysed by boiling with water for 15 minutes, whereas the first two resist hydrolysis under similar conditions. The general stability characteristic of the compounds described as αββ′-tri- and αβββ′-tetra-chlorodiethyl sulphides was therefore remarkable, and the anomaly appeared to merit further investigation.

The percentage of hydrogen found for these compounds by Mann and Pope (see Table I) is considerably too low for αββ′-trichloro- and αβββ′-tetrachloro-diethyl sulphide, but correct for the hexachloro-compound. *ββ′-Dichlorodiethyl sulphide itself gives correct*

TABLE I

Carbon and Hydrogen Analyses.

Compound.	% Required. C.	% Required. H.	% Found. Mann and Pope. C.	% Found. Mann and Pope. H.	% Found. Present authors. C.	% Found. Present authors. H.
ββ′-Dichlorodiethyl sulphide, $C_4H_8Cl_2S$	30·2	5·0	—	—	30·3	5·0
αββ′-Trichlorodiethyl sulphide, $C_4H_7Cl_3S$	24·8	3·6				
αββ′-Trichlorodiethyl sulphide, less two H atoms, $C_4H_5Cl_3S$	25·1	2·6	25·0	2·6	24·7	2·75
αββ′-Trichlorodiethyl sulphoxide, $C_4H_7OCl_3S$	22·9	3·4	22·8	3·4	—	—
αβββ′-Tetrachlorodiethyl sulphide, $C_4H_6Cl_4S$	21·05	2·6				
αβββ′-Tetrachlorodiethyl sulphide, less two H atoms, $C_4H_4Cl_4S$	21·25	1·8	21·2	1·8	21·4	2·0
αβββ′-Tetrachlorodiethyl sulphoxide, $C_4H_6OCl_4S$	19·7	2·5	19·6	2·5	—	—
ααβββ′-Hexachlorodiethyl sulphide, $C_4H_4Cl_6S$	16·2	1·4	16·3	1·3	16·1	1·5

hydrogen analyses, and this fact, coupled with the correct analysis given for the hexachloro-compound, again places the tri- and the tetra-chloro-compound in an anomalous position. Further,

αββ'-trichloro- and αβββ'-tetrachloro-diethyl sulphoxide give, according to Mann and Pope, hydrogen analyses agreeing with those demanded by theory. These sulphoxides, however, were not prepared from the corresponding sulphides by oxidation, but were obtained from ββ'-dichlorodiethyl sulphoxide, $(CH_2Cl{\cdot}CH_2)_2SO$, by chlorination with hypochlorite solution.

As shown in Table I, we have repeated the carbon and hydrogen analyses of the tri-, tetra-, and hexa-chloro-compounds and have obtained values agreeing with those of Mann and Pope. It would seem, therefore, that the lowness of the observed hydrogen content of the tri- and the tetra-chloro-compound can be explained only on the assumption that these two substances actually do contain less hydrogen, and that they have in fact the empirical formulæ $C_4H_5Cl_3S$ and $C_4H_4Cl_4S$, respectively, instead of the formulæ $C_4H_7Cl_3S$ and $C_4H_6Cl_4S$ assigned to them by Mann and Pope.

The chlorine content of the compounds calls for some comment. The compound $C_4H_7Cl_3S$ requires 55·0% of chlorine, $C_4H_6Cl_4S$ 62·2%, $C_4H_5Cl_3S$ 55·6%, and $C_4H_4Cl_4S$ 62·8%. Analyses made by us show that the tri- and the tetra-chloro-compound actually contain 55·6% and 62·8% of chlorine, respectively, and not 55·0% and 62·2% as stated by Mann and Pope. The lower percentages of chlorine are, however, readily and repeatedly obtainable, since, owing to the great stability of the two compounds, it is only by the most protracted heating that the last traces of chlorine can be removed from them when the halogen is being estimated by the Carius method. The tetrachloro-compound gave 62·1% of chlorine after being heated at 300° for 12 hours, 62·4% after 20 hours, and 62·7% after about 60 hours. A concurrent blank experiment showed that this increase was not due to removal of halogen from the glass of the bomb tube itself.

Ultimate analysis thus appears to indicate that the tri- and the tetra-chloro-compound in question contain two hydrogen atoms less than stated by Mann and Pope, and it is suggested that they are the vinyl derivatives (I) $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}CCl{:}CHCl$ (or $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}CH{:}CCl_2$) and (II) $CH_2Cl{\cdot}CH_2{\cdot}S{\cdot}CCl{:}CCl_2$ respectively. Compounds of this type, containing an accumulation of halogen atoms around a double bond, should be less readily hydrolysed than the corresponding saturated compounds.

Further support for these constitutions is afforded by the behaviour of the substances towards concentrated sulphuric acid. Both the tri- and the tetra-chloro-compound give deep red colorations, visible at very great dilutions, on treatment with this reagent, whereas the di- and the hexa-chloro-compound give negative results.

The presence of a double bond in the tri- and the tetra-chloro-com-

pound is confirmed by a study of their parachors. From the values given by Sugden (J., 1924, **125**, 1177, 1525, and subsequent papers), for the atomic and structural constants it is evident that the decrease in parachor resulting from the loss of two hydrogen atoms is greater than the increase due to the consequent introduction of a non-polar double bond, or the formation of a three-, four-, or five-membered ring. The observed values of the parachors (Table II) are considerably less than those calculated for the compounds $C_4H_7Cl_3S$

TABLE II.

Calculated and Observed Parachors.

The calculated parachors are obtained by the summation of the requisite atomic and structural constants (Sugden, *loc. cit.*), and the observed parachors from the expression $M \times \gamma^{\frac{1}{4}}/D$, where M is the assumed molecular weight, γ the surface tension and D the density, both at the same temperature.

Formula.	[P] calc.	M.	[P] obs.
Trichloro-compound.			
$C_4H_7Cl_3S$	350·0	193·5	341·9
$C_4H_5Cl_3S$ containing:			
(*a*) 5-membered ring	324·3	191·5	338·4
(*b*) 4-membered ring	327·4		
(*c*) 3-membered ring	332·5		
(*d*) non-polar double bond	339·0		
Tetrachloro-compound.			
$C_4H_6Cl_4S$	387·2	228·0	377·4
$C_4H_4Cl_4S$ containing:			
(*a*) 5-membered ring	361·5	226·0	374·1
(*b*) 4-membered ring	364·6		
(*c*) 3-membered ring	369·7		
(*d*) non-polar double bond	376·2		

and $C_4H_6Cl_4S$, and are, within the limits of experimental accuracy, identical with those required for the compounds $C_4H_5Cl_3S$ and $C_4H_4Cl_4S$, each containing a non-polar double bond, *i.e.*, for compounds having the structural formulæ (I and II) suggested above. Association does not account for the lowness of the experimental values, for the liquids have normal molecular weights, determined cryoscopically in benzene. Differentiation in this way between the alternative formulæ for the trichloro-compound is not possible, since position isomerism has no effect on the magnitude of the parachor.

Finally, the gradation of other physical properties in the series ββ'-dichlorodiethyl sulphide–trichloro-compound–tetrachloro-compound is more in harmony with the present view of the constitutions of the latter two compounds than with that accepted by Mann and Pope. This is particularly evident when a comparison is made with an analogous chlorinated series, such as, for example, that based on

ethylene dichloride as parent substance. If the tri- and the tetrachloro-compound are simple substitution derivatives of ββ′-dichlorodiethyl sulphide, the gradation of properties might be expected to correspond approximately with that in the series ethylene dichloride–trichloroethane–*s*-tetrachloroethane. If, on the other hand, the compounds in question are chlorinated but unsaturated derivatives of ββ′-dichlorodiethyl sulphide, the corresponding chlorinated hydrocarbon series would be ethylene dichloride–trichloroethylene–perchloroethylene. From Table III it is immediately apparent that

TABLE III.

Comparison of Physical Properties.

Compound.	B. p.	$D_{4°}^{20°}$.	M/D.	Diff.	$\eta_{20°}$.	Log $\eta \times 10^5$.	Diff.
ββ′-Dichlorodiethyl sulphide series:							
	(15 mm.)						
Dichloro-compound	107°	1·2746	124·7		0·043	3·634	
$(CH_2Cl{\cdot}CH_2)_2S$				+ 9·1			−0·18
Trichloro-compound	107	1·4315	133·8		0·028	3·447	
$C_2H_4Cl{\cdot}S{\cdot}CCl{:}CHCl$				+13·2			+0·144
Tetrachloro-compound	124	1·537	147·0		0·039	3·591	
$C_2H_4Cl{\cdot}S{\cdot}CCl{:}CCl_2$							
Ethylene dichloride series:							
(*a*) Chlorine substitution with unsaturation.							
	(760 mm.)						
Ethylene dichloride	84	1·252	70·0		0·0084	2·924	
$CH_2Cl{\cdot}CH_2Cl$				+10·0			−0·132
Trichloroethylene	88	1·477	80·0		0·006	2·792	
$CCl_2{:}CHCl$				+13·2			+0·162
Perchloroethylene	121	1·623	102·2		0·009	2·954	
$CCl_2{:}CCl_2$							
(*b*) Simple chlorine substitution.							
	(700 mm.)						
Ethylene dichloride	84	1·252	79·0		0·0084	2·924	
$CH_2Cl{\cdot}CH_2Cl$				+13·4			+0·145
Trichloroethane	114	1·443	92·4		0·012	3·079	
$CHCl_2{\cdot}CH_2Cl$				+12·5			+0·151
s-Tetrachloroethane	146	1·600	104·9		0·017	3·230	
$CHCl_2{\cdot}CHCl_2$							

the latter alternative is more in keeping with the facts. The very small increase in boiling point on passing from ββ′-dichlorodiethyl sulphide to the trichloro-derivative (so inappreciable under reduced pressures as to preclude separation of the two compounds by fractional distillation), the diminished increment in molecular volume (M/D) at 20°, and the decrease in viscosity (η), followed in each case by normal increments on passing to the tetrachloro-compound, all find their parallel in the series ethylene dichloride–trichloroethylene–perchloroethylene, and are in striking contrast with the regular progression in properties characteristic of a simple substitution series such as ethylene dichloride–trichloroethane–*s*-tetrachloroethane.

The whole of the evidence indicates that the products of chlorination of ββ′-dichlorodiethyl sulphide described by Mann and Pope

as αββ′-tri- and αβββ′-tetra-chlorodiethyl sulphides are in reality di- and tri-chlorovinyl β-chloroethyl sulphides respectively.

It is proposed to attempt the synthesis of the true αββ′-tri- and αβββ′-tetra-chlorodiethyl sulphides by condensing β-chloroethyl mercaptan with mono- and di-chloroacetaldehyde in the presence of hydrogen chloride.

EXPERIMENTAL.

Preparation and Analysis.—The chlorination of ββ′-dichlorodiethyl sulphide and the separation of the products of chlorination were effected in the manner described by Mann and Pope (*loc. cit.*), the tetrachloro-compound being for convenience prepared by the direct chlorination of the trichloro-compound previously obtained. The individual products were subsequently purified by repeated fractional distillation through a Dufton column at 15 mm. pressure and obtained as colourless liquids.

(1) *ββ′-Dichlorodiethyl sulphide*: *M* in benzene, 158; m. p 14·4°; b. p. 107°/15 mm. (Steinkopf, Herold, and Stöhr, *Ber.*, 1920 **53**, 1007, give 108°/15 mm.) (Found: C, 30·3; H, 5·0; Cl, 44·6 Calc.: C, 30·2; H, 5·0; Cl, 44·6%; *M*, 159).

(2) *Trichloro-compound*: *M* in benzene, 190; b. p. 107°/15 mm (Mann and Pope, *loc. cit.*, give 106·5—108°/15 mm.) (Found C, 24·75, 24·7; H, 2·75, 2·75; Cl, 55·5, 55·8. Calc. for $C_4H_5Cl_3S$ C, 25·1; H, 2·6; Cl, 55·6%; *M*, 191·5).

(3) *Tetrachloro-compound*: *M*, in benzene, 225; b. p. 124°/15 mm (Mann and Pope, *loc. cit.*, give 123—125°/15 mm.) (Found: C, 21·[illegible] 21·45; H, 2·0, 2·05; Cl, 62·6, 62·8. Calc. for $C_4H_4Cl_4S$: C, 21·2[illegible] H, 1·8; Cl, 62·8%; *M*, 226).

(4) *ααβββ′-Hexachlorodiethyl sulphide*: *M*, in benzene, 297 b. p. 160°/15 mm. (Mann and Pope, *loc. cit.*, give 160—161°/15 mm (Found: C, 16·1; H, 1·5; Cl, 71·6. Calc. for $C_4H_4Cl_6S$: C, 16·[illegible] H, 1·4; Cl, 71·7%; *M*, 297).

The chlorine values for the tri- and the tetra-chloro-compoun respectively, were obtained after 12 and 60 hours' heating at 30[illegible]

Hydrolysis.—A comparison of the rates of hydrolysis was ma by refluxing approximately 0·12 g. of each of the substances wi 50 c.c. of water for 15 minutes and rapidly titrating the liberat acid with standard bartya solution (Found: Cl, 43·6, 3·6, 2·6, a 17·25% for the di-, tri-, tetra-, and hexa-chloro-compour respectively).

Densities.—The densities of ββ′-dichlorodiethyl sulphide and of t tri- and the tetra-chloro-compound were determined at 20° and [illegible] with a calibrated density bottle of approximately 5 c.c. capaci The values obtained are in good agreement with those recorded the literature (Mann and Pope, *loc. cit.*; Wilkinson and Wernlu

J. Amer. Chem. Soc., 1920, **42**, 1382): ββ'-dichlorodiethyl sulphide, $D_{4^\circ}^{20^\circ}$ 1·2746, $D_{4^\circ}^{25^\circ}$ 1·2693; trichloro-compound, $D_{4^\circ}^{20^\circ}$ 1·4315, $D_{4^\circ}^{25^\circ}$ 1·4255; tetrachloro-compound, $D_{4^\circ}^{20^\circ}$ 1·537, $D_{4^\circ}^{25^\circ}$ 1·531.

The densities and boiling points of the chlorinated hydrocarbons quoted for comparison in Table III are taken from the International Critical Tables, Vol. I (National Research Council, U.S.A., 1926).

Surface Tensions.—The surface tensions of the compounds were measured by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 860; 1924, **125**, 27). The bubblers employed were calibrated as described in the reference quoted, their constants being :

Apparatus	1	2	3	4
K_1	0·01325	0·01403	0·01339	0·01981
R_2 (cm.)	0·1219	0·1215	0·1110	0·1071
$K_2 = 0{\cdot}69\ R_2 g$	82·51	82·24	75·14	72·5

Apparatus	5	6	7
K_1	0·01475	0·01055	0·02664
R_2 (cm.)	0·1215	0·1433	0·0796
$K_2 = 0{\cdot}69\ R_2 g$	82·24	96·97	53·88

The surface tension (γ) is obtained from the equation $\gamma = K_1(P + K_2D)$, and the parachor calculated from the expression $M\gamma^{\frac{1}{4}}/(D - d)$, where P is the difference in the pressures required to liberate bubbles from the two tubes, expressed in dynes/cm.^{2}, D and d are the densities of the liquid and vapour respectively at the temperature of measurement in g./c.c., and M is the molecular weight.

Trichloro-compound (M = 191·5).

Temp.	App. No.	P.	K_2D.	γ.	Parachor.
20°	4	1963	104	40·9	338·3
25	7	1430	76	40·1	338·1
25	2	2656	117	40·3	338·5
25	6	3669	138	40·2	338·3
30	3	2871	107	39·9	339·1
					Mean 338·4

Tetrachloro-compound (M = 226).

Temp.	App. No.	P.	K_2D.	γ.	Parachor.
20	6	3799	149	41·7	373·6
20	5	2735	126	42·2	374·8
20	1	3041	127	42·0	374·3
25	6	3752	149	41·2	374·0
25	5	2668	126	41·2	374·0
					Mean 374·1

Viscosities.—The viscosities of ββ'-dichlorodiethyl sulphide and of the tri- and the tetra-chloro-compound were determined at 20° in an Ostwald viscometer by the method of Scarpa (*Gazzetta*, 1910, **40**, ii, 261). The instrument was calibrated with water, and the calibration checked by means of purified benzene and carbon tetrachloride.

The viscosities of trichloroethylene, trichloroethane, and *s*-tetra-

chloroethane were similarly determined. Those given in Table III *for ethylene dichloride* and perchloroethylene are the values obtained by *Thorpe* and Rodger and quoted in Landolt–Börnstein–Roth "Tabellen" (4 Auflage, 1912).

Summary.

Analytical, chemical, and physical data are given in support of the view that the products of chlorination of ββ'-dichlorodiethyl sulphide described by Mann and Pope (J., 1922, **121**, 594) as αββ'-tri- and αβββ'-tetra-chlorodiethyl sulphides are in reality dichloro- and trichloro-vinyl β-chloroethyl sulphides, respectively.

Sir W. J. Pope and Dr. F. G. Mann have read the manuscript of this paper and concur in the general conclusion that their tri- and *tetra-chlorodiethyl sulphides are really substituted vinyl ethyl sulphides, but adhere to the disposition of the* chlorine atoms which they previously suggested.

We desire to express our thanks to Major W. C. Ball, O.B.E., D.Sc., for facilities placed at our disposal and for much helpful criticism.

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XXIII.—*Studies in Colour and Constitution. Part II. Further Observations on the Effect of Substituents on the Colour of Azo-dyes.*

By HERBERT HENRY HODGSON and FREDERICK WILLIAM HANDLEY.

AZO-DYES with Schäffer's salt or R-salt as the second component have been prepared from the bases IX—XX named on p. 165 and have been included, together with those described in Part I (J., 1926, 542), in a scheme showing the effects of the substituents on the colour of the dyes.

By dyeings on wool and colorimetric estimations of the dye solutions with the Lovibond tintometer, the powerful bathochromic influence of a methylthiol group in the para-position with respect to the azo-group and the almost equally powerful influence of an *o*-methoxy-group have been further demonstrated, and a less powerful but still pronounced bathochromic influence has been established for chlorine in the para-position. In the ortho- or meta-position, especially in the latter, chlorine produces a hypsochromic effect, which is manifested in the colours of the dyes prepared from the bases containing 2 : 4- and 2 : 5-dichloro-, 2-chloro-

4-methoxy-, 5-chloro-2-methoxy-, and 5-chloro-2-methylthiol substituents.

The mass of the substituent appears to affect the colour developed by the dye in concentrated sulphuric acid solution.

EXPERIMENTAL.

Initial Materials.—By prolonging the time of nitration from 10 to 25 minutes 2 : 4-dichloronitrobenzene was prepared in 88% yield by Roberts and Turner's method (J., 1925, **127**, 2011). It was converted almost quantitatively into 2 : 4-dimethoxynitrobenzene, m. p. 74°, by the action of methyl-alcoholic sodium methoxide. Reduction of this (4 g.) with iron powder (8 g.), glacial acetic acid (5 c.c.), and water (20 c.c.) gave 2 : 4-dimethoxyaniline (2·4 g.), m. p. 39°. Reduction with tin (4 g.) and conhydrochloric acid (20 c.c.) gave an oily chlorinated product the acetyl derivative of which crystallised from alcohol or dilute acetic acid in colourless needles, m. p. 142° (Found : Cl, 15·5. Calc. for $C_{10}H_{12}O_3NCl$: Cl, 15·5%), and was probably 6-chloro-2 : 4-dimethoxyacetanilide.

4-Chloro-2-thioanisidine.—A solution of 3-chloro-6-nitrothioanisole (2·8 g.) (Hodgson and Handley, *J. Soc. Chem. Ind.*, 1927, 46, 435T) in glacial acetic acid (10 c.c.) containing tin (4 g.) was cautiously heated while concentrated hydrochloric acid (10 c.c.) was being gradually added. After 30—45 minutes, the mixture was heated on a boiling water-bath for 10 minutes, and then steam-distilled after being made alkaline with sodium hydroxide; 4-chloro-2-thioanisidine (1·5 g.) was thus obtained as an oil in the distillate. Its aqueous solution gave an orange colour with bleaching powder and a bluish-green colour with ferric chloride. The *acetyl* derivative crystallised from water or dilute acetic acid in colourless needles, m. p. 110° (Found : N, 6·6; Cl, 16·3. $C_9H_{10}ONClS$ requires N, 6·5; Cl, 16·5%), and the *benzoyl* derivative from alcohol in colourless needles, m. p. 106° (Found : Cl, 12·7. $C_{14}H_{12}ONClS$ requires Cl, 12·8%).

4 : 4'-Dinitro-5 : 5'-dimethylthioldiphenyl disulphide was obtained by carefully adding aqueous sodium disulphide (crystallised sodium sulphide, 2·4 g.; sulphur, 0·32 g.; water, 5 c.c.) to a hot solution of 3-chloro-6-nitrothioanisole (4 g.) in alcohol (100 c.c.), boiling the mixture under reflux for 6 hours, and removing unchanged material by steam-distillation; the non-volatile product crystallised from glacial acetic acid, in which it was sparingly soluble, in pale yellow needles, m. p. 216—217° (Found : S, 31·8. $C_{14}H_{12}O_4N_2S_4$ requires S, 32·0%). It is insoluble in alcohol and very sparingly soluble in acetone.

2 : 4-Dimethylthiolnitrobenzene was prepared by heating together a suspension of the above disulphide (2 g.) in alcohol (10 c.c.) and a solution of crystallised sodium sulphide (1 g.) and sodium hydroxide (2·4 g.) in water (12 c.c.) for 10 minutes and then cooling the deep brown solution, diluting it with water (30 c.c.) and treating it with methyl sulphate (2·5 c.c.), whereupon the thioether (1·9 g.) separated immediately. It crystallised from alcohol, acetone, or acetic acid in yellow, curved needles, m. p. 113° (Zincke and Krüger, *Ber.*, 1912, **45**, 3474, give m. p. 114° for a product obtained by the nitration of *m*-dimethylthiolbenzene) (Found: N, 6·5. Calc.: N, 6·5%). It was also obtained in a similar manner but in poorer yield from 1 : 1'-dinitrodiphenyl 2 : 2' : 4 : 4'-tetrasulphide (Hodgson and Handley, *loc. cit.*).

2 : 4-*Dimethylthiolaniline* was obtained from 2 : 4-dimethylthiolnitrobenzene by reduction with tin and hydrochloric and acetic acids. It is a colourless oil with a geranium-like odour and is readily volatile in steam. The *hydrochloride* crystallises from water in colourless needles which rapidly turn blue on exposure to light (Found: N, 6·5. $C_8H_{11}NS_2,HCl$ requires N, 6·3%), and give a deep blue colour with ferric chloride. The *acetyl* derivative crystallises from alcohol or dilute acetic acid in silky needles, m. p. 114° (Found: S, 28·2. $C_{10}H_{13}ONS_2$ requires S, 28·1%), and the *benzoyl* derivative from alcohol in colourless needles, m. p. 125° (Found: S, 22·2. $C_{15}H_{15}ONS_2$ requires S, 22·1%).

3 : 3'-*Diacetamido*-4 : 4'-*dinitrodiphenyl Disulphide*.—3-Chloro-6-nitroaniline was first prepared by heating (6—7 hours) 2 : 4-dichloronitrobenzene (8 g.) with alcohol (10 c.c.) and aqueous ammonia (35 c.c.; *d* 0·880) in a sealed tube at 160—165°; the mixture was then diluted with water and the product (7 g.) filtered off. The chlorine in 3-chloro-6-nitroaniline is very stable towards alcoholic sodium disulphide, whereas in 3-chloro-6-nitroacetanilide, obtained by acetylation with a mixture of acetic anhydride (which alone only partly acetylates the base) and acetyl chloride, the chlorine is again labile and readily reacts with sodium disulphide to form 3 : 3'-*diacetamido*-4 : 4'-*dinitrodiphenyl disulphide*; this crystallises from glacial acetic acid in pale yellow needles, m. p. 192—193° (Found: N, 13·1; S, 15·3. $C_{16}H_{14}O_6N_4S_2$ requires N, 13·3; S, 15·2%), and is insoluble in alcohol and benzene and only slightly soluble in acetone.

6-*Nitro*-3-*thioanisidine* was obtained from the corresponding disulphide (above) by the method described for the preparation of 2 : 4-dimethylthiolnitrobenzene, and crystallised from alcohol in deep yellow needles, m. p. 116° (Found: S, 17·7. $C_7H_8O_2N_2S$ requires S, 17·4%).

Results.

The order of increasing redness is from left to right. Brackets indicate almost identical shades.

Dye.	Experiment.	Order.																			
From Schäffer's salt.	Wool dyeing.	V	XV	XIV	VIII	XVIII	III	I	XIX	XVI	VII	XVII	VI	II	IV	XI	XII	XX	IX	X	XIII
		(Reddish-violet)	Bluish-red)		(Red	)				Scarlet to reddish-orange					)	(	Orange to orange-yellow				)
,, ,, ,,	Lovibond.	V	XIV	XV	VIII	XVIII	VI	III	I	IV	XIX	VII	II	XVI	XVII	XII	XI	XX	IX	XIII	X
,, ,, ,,	Sulphuric acid.	XIV (	XVIII Blue	VIII	V)	XVI (	VI	XIX	XVII Violet	VII	XV	IV)	II (	III	I Crimson	XII	XI	XIII)	IX (Scarlet)	XX (Reddish-orange)	X (Orange)
From R-salt	Wool dyeing.	V	XIV	XV	VIII	XVIII	III	I	XIX	VI	II	VII	XVI	IV	XVII	XI	XII	XX	IX	X	XIII
		(Violet)	(Reddish-violet)		(Bluish-red)	(			Red with gradual increase of yellow							X	Orange with increase of yellow				)
,, ,,	Lovibond.	V	XV	XIV	XVIII	VIII	III	I	VI	XIX	IV	II	VII	XVI	XII	XVII	XI	XX	IX	XIII	X
,, ,,	Sulphuric acid.	XIV	XVIII Blue	VIII	V)	VII	VI	XVI	XIX Violet	XVII	IV	XV)	II (	III	I	XII Crimson	XIII	XI	IX)	XX (Reddish-orange)	X

Combined Effects of the Substituents deduced from the Dyeing Results.

A denotes a resultant additive effect, S a resultant subtractive effect.

Groups in the basic component.	Effect on depth of shade. Dye from Schäffer's salt.	Dye from R-salt.
2-Chloro-4-methoxy	2-Cl, no effect	S
4- ,, -2- ,, ...	A	4-Cl, no effect
5- ,, -2- ,, ...	S	S
2- ,, -4-methylthiol	S (slightly)	S (slightly)
4- ,, -2- ,, ...	4-Cl, no effect	A
5- ,, -2- ,, ...	S	S

Groups in the basic component.	Effect on depth of shade. Dye from Schäffer's salt.	Dye from R-salt.
2-Methoxy-4-methylthiol	A (optimum effect)	A (optimum effect)
4- ,, -2- ,, ...	A	A
2 : 4-Dimethoxy	A	A
2 : 4-Dimethylthiol	A	A
2 : 4-Dichloro	S	S
2 : 5- ,, ...	A (hypsochromic)	A (hypsochromic)

3-Chloro-4-nitrothioanisole, prepared by the Sandmeyer method from 6-nitro-3-thioanisidine, is slowly volatile in steam and crystallises from alcohol in pale yellow needles, m. p. 61° (Found: Cl, 17·2. $C_7H_6O_2NClS$ requires Cl, 17·4%).

2-Chloro-4-thioanisidine, prepared by reduction of the preceding nitro-compound with tin and hydrochloric acid, is an oil. The *hydrochloride* crystallises from water in long needles, m. p. 217—218°, and gives a reddish-purple colour with ferric chloride. The *acetyl* derivative separates from dilute acetic acid in long needles, m. p. 129° (Found: Cl, 16·3; S, 15·2. $C_9H_{10}ONClS$ requires Cl, 16·5; S, 14·8%).

The Dyes, Dyeing Trials, and Dye Solutions.—These were made by the methods described in the previous paper (*loc. cit.*). For convenience, each dye is referred to by the attached numeral, which indicates the amine employed in its preparation: 2-anisidine (I), 4-anisidine (II), 4-chloro-2-anisidine (III), 2-chloro-4-anisidine (IV), 2-anisidine-4-methyl thioether (V), 4-anisidine-2-methyl thioether (VI), 2-thioanisidine (VII), 4-thioanisidine (VIII), 2-chloroaniline (IX), 3-chloroaniline (X), 4-chloroaniline (XI), 2 : 4-dichloroaniline (XII), 2 : 5-dichloroaniline (XIII), 2 : 4-dimethylthiolaniline (XIV), 2 : 4-dimethoxyaniline (XV), 4-chloro-2-thioanisidine (XVI), 5-chloro-2-thioanisidine (XVII), 2-chloro-4-thioanisidine (XVIII), 5-chloro-2-anisidine (XIX), aniline (XX).

The authors desire to thank Mr. H. Wilkinson for advice concerning the estimations with the Lovibond tintometer and the colour interpretations, and the British Dyestuffs Corporation for gifts of chemicals.

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XXIV.—*The Reactivity of the Double Bond in Coumarins and Related αβ-Unsaturated Carbonyl Compounds. Part I. Addition of Cyanoacetamide to Coumarins.*

By TIRUVENKATA RAJENDRA SESHADRI.

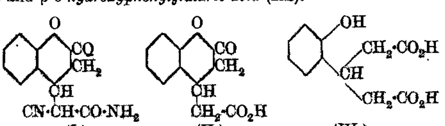
THE unsaturated centre in coumarin seems to differ greatly in reactivity from the double bond in related compounds such as cinnamic acid and ethyl cinnamate. For instance, sodium bisulphite combines readily in a few minutes with coumarin, whereas with cinnamic acid under comparable conditions the combination remains incomplete even after 12 hours. This question of the reactivity of the double

bond in coumarins in comparison with other αβ-unsaturated carbonyl compounds has not hitherto been systematically investigated.

The interaction of cyanoacetamide and coumarins is of much interest from the theoretical point of view and incidentally offers a method for the preparation of a series of reduced coumarin derivatives containing asymmetric carbon atoms. When heated in alcoholic solution in the presence of piperidine, coumarin and cyanoacetamide react additively in equimolecular proportion at the double bond. The reaction is complete in about 6 hours; but in similar circumstances, although the heating was continued for 40—50 hours, cinnamic acid, ethyl cinnamate and even coumaric acid yielded no detectable quantity of additive products, the original substances being recovered unchanged. Hence it appears at first sight that the reactivity of the double bond in coumarin is greatly enhanced as the result of its situation in a ring structure.

Nevertheless, this explanation of the enhanced reactivity of coumarin as compared with ethyl cinnamate, although considered to be a part of the truth, is probably inadequate; a further important factor is doubtless connected with the degree of neutralisation of the ketonic properties of the carbonyl group by the singly bound oxygen atom. In coumarin, the aromatic nucleus makes demands of the attached oxygen, reducing the capacity of this atom for neutralising the carbonyl group. Electronic mechanisms embodying this suggestion have been put forward by Robinson. Thus coumarin should occupy a position intermediate between a typical alkyl cinnamate and a typical alkyl styryl ketone. The relative importance of the parts played by the cyclic structure and the conjugation of the oxygen atom with the nucleus could be estimated from the results of a comparative study of the reactions of alkyl and aryl cinnamates, and it is proposed to continue the investigation in this direction.

3 : 4-*Dihydrocoumarin-4-cyanoacetamide* (I) is readily hydrolysed by boiling concentrated hydrochloric acid or 10% caustic potash solution with the formation of 3 : 4-*dihydrocoumarin-4-acetic aci* (II) and β-o-*hydroxyphenylglutaric acid* (III).



(I.) (II.) (III.)

The relationship of these acids was established by their interconversion. At its melting point, (III) decomposes with the

evolution of water and forms (II). The lactone (II) or the hydroxy-acid (III) can be obtained from an alkaline solution of either according as the solution is strongly acidified and warmed or is rendered just acid and kept cold. Intermediate stages represented by 3 : 4-*dihydrocoumarin-4-cyanoacetic acid* (IV) and 3 : 4-dihydrocoumarin-4-carbamylacetic acid (V) were isolated only in cases where hydrolysis in stages with cold concentrated hydrochloric acid was possible.

(IV.)

(V.)

Alkyl and halogen substituents in the pyrone ring, as in 4 : 7-dimethylcoumarin, 3-methylcoumarin, and 3-bromocoumarin, completely inhibit the addition. But their presence in the benzene ring has not yet been found to offer any hindrance and the addition takes place with almost as much ease as in the case of coumarin. 7-Methylcoumarin yields a product which resembles in every respect dihydrocoumarincyanoacetamide and gives rise to the same series of hydrolytic products. 6-Aminocoumarin, a golden-yellow solid, forms a colourless additive compound with cyanoacetamide, whereas the product from the colourless 6-nitrocoumarin is deep yellow.

6-*Nitro*-3 : 4-*dihydrocoumarin-4-cyanoacetamide* was unaffected by cold concentrated hydrochloric acid and hence stepwise hydrolysis was not possible; only 6-*nitro*-3 : 4-*dihydrocoumarin-4-acetic acid* could be obtained in a pure condition from the products of hydrolysis. This acid is colourless and gives colourless solutions in organic solvents and in aqueous acid; on the other hand, its solutions in water, especially hot water, and in aqueous alkali are yellow. In all probability these yellow solutions contain the nitrophenolic acid $NO_2{\cdot}C_6H_3(OH){\cdot}CH(CH_2{\cdot}CO_2H)_2$, which could only be isolated in the form of its *disilver* salt.

EXPERIMENTAL.

3 : 4-*Dihydrocoumarin-4-cyanoacetamide* (I).—A solution of coumarin (3 g.), cyanoacetamide (2 g.), and a few drops of piperidine in alcohol (30 c.c.) was kept at the point of incipient ebullition for 6 hours. The cooled liquid slowly deposited a mass of colourless crystals, which were washed with cold alcohol (yield, 4 g.; m. p. 215—216°). The substance was slightly soluble in boiling water and readily soluble in boiling alcohol, chloroform or benzene, crystallising on cooling in flat, colourless needles, m. p. 219—220°

(decomp.) (Found: C, 62·8; H, 4·4; N, 12·4. $C_{12}H_{10}O_3N_2$ requires C, 62·6; H, 4·4; N, 12·2%). It was insoluble in aqueous sodium carbonate or ammonia, but dissolved slowly in dilute aqueous sodium hydroxide with the production of ammonia.

3 : 4-*Dihydrocoumarin*-4-*cyanoacetic Acid* (IV).—A mixture of dihydrocoumarincyanoacetamide (1 g.) and cold concentrated hydrochloric acid (5 c.c.) was vigorously shaken, giving a clear solution which soon deposited a colourless, crystalline precipitate. This crystallised from much water or alcohol in colourless, hexagonal plates, m. p. 226—227° (Found: C, 62·6; H, 4·1; N, 6·1. $C_{12}H_9O_4N$ requires C, 62·3; H, 3·9; N, 6·1%).

Dihydrocoumarincyanoacetic acid underwent further hydrolysis when boiled with concentrated hydrochloric acid, dilute aqueous sodium hydroxide or even ammonia, so that when the silver salt was prepared in the usual way by means of ammonium hydroxide and silver nitrate the disilver salt of β-*o*-hydroxyphenylglutaric acid (below) was produced.

3 : 4-*Dihydrocoumarin*-4-*acetic Acid* (II).—Dihydrocoumarincyanoacetamide (1 g.) was boiled with concentrated hydrochloric acid (5 c.c.) for 5 minutes and on cooling *dihydrocoumarinacetic acid* crystallised; a further quantity of it was obtained by evaporating the mother-liquor to dryness and adding a few drops of water to dissolve the ammonium chloride (yield, 0·7 g.). Purification was effected by dissolution in aqueous sodium carbonate and reprecipitation; the acid crystallised from boiling water, alcohol, or benzene in colourless, stout prisms, m. p. 113—114° (Found: C, 64·0; H, 4·8. $C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%). This acid was obtained also by the hydrolysis of dihydrocoumarincyanoacetamide (1 g.) with aqueous potassium hydroxide (2 g. in 10 c.c. of water) at the boiling point for a few minutes; the clear solution was acidified with hydrochloric acid and evaporated to dryness. Enough water was then added to dissolve the inorganic salts, leaving an almost pure specimen of dihydrocoumarinacetic acid (yield, 0·75 g.). The silver salt of this acid could not be obtained by the usual method, since the product was found on analysis to be the disilver salt of β-*o*-hydroxyphenylglutaric acid described below.

β-o-*Hydroxyphenylglutaric Acid* (III).—This acid was obtained whenever dihydrocoumarinacetic acid was prepared. When the mother-liquor after the separation of the acetic acid was kept for several hours, stout, colourless crystals of the glutaric acid separated. The best method of preparation is to dissolve dihydrocoumarinacetic acid in dilute aqueous sodium carbonate and then to render the solution just acid and keep it cold for several hours; colourless, stout crystals are slowly deposited. The *acid*

is sparingly soluble in ether or benzene; it is easily soluble in boiling water, alcohol, or acetone, and crystallises in colourless cubes melting at 160° with evolution of steam and formation of dihydrocoumarinacetic acid (Found: C, 59·2; H, 5·5. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%). Its aqueous solution was strongly acid to litmus and when boiled with dilute hydrochloric acid it underwent conversion into the closed-ring acetic acid. The *disilver* salt was obtained as a colourless, amorphous, bulky precipitate in the usual way by means of ammonia and silver nitrate and when dry was a colourless powder (Found: Ag, 49·0. $C_{11}H_{10}O_5Ag_2$ requires Ag, 49·3%).

7-Methyl-3 : 4-dihydrocoumarin-4-cyanoacetamide.—An alcoholic solution of 7-methylcoumarin (4 g.), cyanoacetamide (2 g.), and a few drops of piperidine was boiled for 15 hours, a shorter period involving admixture of the condensation product with unchanged 7-methylcoumarin. The product (about 4 g.) was fairly soluble in boiling acetone or alcohol and very readily soluble in pyridine, from which it crystallised in colourless, rectangular prisms, m. p. 245° (Found: C, 64·2; H, 5·1; N, 11·8. $C_{13}H_{12}O_3N_2$ requires C, 63·9; H, 4·9; N, 11·5%).

7-Methyl-3 : 4-dihydrocoumarin-4-cyanoacetic acid was obtained from the above compound by treatment with cold concentrated hydrochloric acid. At first a clear solution was produced which soon deposited a colourless, crystalline precipitate; this crystallised from boiling water or alcohol in colourless, rhombic prisms, m. p. 230—232° (Found: N, 5·9. $C_{13}H_{11}O_4N$ requires N, 5·7%).

7-Methyl-3 : 4-dihydrocoumarin-4-acetic acid, which resulted from the hydrolysis of 7-methyldihydrocoumarincyanoacetamide with hot concentrated hydrochloric acid or hot aqueous potash, was easily soluble in boiling water, alcohol, acetone, or benzene and crystallised from these solvents in colourless, rectangular plates, m. p. 111—112° (Found: C, 65·3; N, 5·6. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%).

β-p-Methyl-o-hydroxyphenylglutaric acid was obtained by dissolution of the above lactonic acid in dilute aqueous sodium carbonate and careful acidification of the solution in the cold. The colourless, rectangular prisms that were slowly deposited melted at 148—149° with formation of 7-methyldihydrocoumarinacetic acid. The phenolic acid is sparingly soluble in benzene, but dissolves readily in boiling water, alcohol, or acetone (Found: C, 60·3; H, 5·9. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%). The disilver salt, which was a colourless powder, was identical with those resulting from the cyanoacetic and acetic acids mentioned above (Found: Ag, 47·4. Calc.: Ag, 47·7%).

6-Nitro-3 : 4-dihydrocoumarin-4-cyanoacetamide (VI).—Golden-

yellow crystals were deposited when an alcoholic solution of 6-nitrocoumarin (3 g.), cyanoacetamide (1·5 g.), and a few drops of piperidine was gently boiled for 4 hours (yield, about 3·5 g.). The substance was sparingly soluble in benzene, acetone, or alcohol and readily soluble in boiling pyridine, from which it separated in golden-yellow plates which neither melted nor decomposed below 300° (Found: N, 15·6. $C_{12}H_9O_5N_3$ requires N, 15·3%). *Nitrodihydrocoumarincyanoacetamide* was only very slowly affected by cold dilute hydrochloric acid or sodium hydroxide; on boiling with the alkali, however, solution took place with the evolution of ammonia.

6-*Nitro*-3 : 4-*dihydrocoumarin*-4-*acetic Acid* (VII).—A boiling mixture of nitrodihydrocoumarincyanoacetamide (1 g.) and concentrated hydrochloric acid (10 c.c.) gradually deposited a white, crystalline precipitate. This dissolved in cold dilute aqueous sodium carbonate to a deep yellow solution, which, when rendered strongly acid, turned colourless and *nitrodihydrocoumarinacetic acid* soon separated in colourless, rhombic prisms, m. p. 205° (decomp.) (Found: N, 5·8. $C_{11}H_9O_6N$ requires N, 5·6%). The acid dissolved very sparingly in benzene or chloroform and was slightly soluble in alcohol; these solutions were perfectly colourless, even on boiling. The aqueous solution, however, was yellow and the colour deepened on boiling; introduction of a trace of any alkali rendered it deep yellow, whereas the addition of mineral acid not only removed the colour but caused the precipitation of the acid. The silver salt prepared by the usual method was obtained as a light yellow powder and on analysis was found to be the *disilver* salt of the open-chain phenolic glutaric acid (Found: Ag, 44·3. $C_{11}H_9O_7NAg_2$ requires Ag, 44·7%).

6-*Amino*-3 : 4-*dihydrocoumarin*-4-*cyanoacetamide*.—The best yield of this product was obtained by boiling an alcoholic solution of 6-aminocoumarin (2 g.), cyanoacetamide (1 g.), and a few drops of piperidine for 6 hours. Longer heating produced a resin and the yield was lowered when the period of reaction was shortened. The solid was isolated and washed with hot alcohol to remove unchanged aminocoumarin. The product was sparingly soluble in chloroform, benzene, or alcohol and crystallised from pyridine in colourless prisms, m. p. 270° (decomp.) (yield, 1·5 g.) (Found: C, 59·0; H, 4·4; N, 17·4. $C_{12}H_{11}O_3N_3$ requires C, 58·7; H, 4·5; N, 17·1%). A yellow solution in dilute aqueous sodium hydroxide is formed slowly in the cold and readily on boiling, ammonia being evolved; the substance is also readily soluble in dilute or concentrated hydrochloric acid. The formulation of this compound as an analogue of dihydrocoumarincyanoacetamide is justified by the observation

that the addition product is a primary aromatic amine. The corresponding diazonium salt couples with β-naphthol to give a scarlet-red azo-compound that dissolves in concentrated sulphuric acid to a crimson solution.

The *benzoyl* derivative was obtained by carrying out the benzoylation in the presence of dilute aqueous sodium carbonate. It was sparingly soluble in alcohol and crystallised from pyridine in colourless, flat needles, m. p. 300° (decomp.) (Found : C, 65·1; H, 4·4. $C_{19}H_{15}O_4N_3$ requires C, 65·3; H, 4·3%).

6-Amino-3 : 4-dihydrocoumarin-4-carbamylacetic Acid.—A solution of 6-aminodihydrocoumarincyanoacetamide (1 g.) in cold concentrated hydrochloric acid (10 c.c.) remained clear until it was heated just to boiling. Immediately precipitation started and a good yield of colourless, rectangular rods was obtained on cooling. The product was washed with cold concentrated hydrochloric acid and finally with alcohol; m. p. 225° (decomp.) (Found : C, 48·1; H, 4·4; N, 9·3; Cl, 11·9. $C_{12}H_{13}O_5N_2Cl$ requires C, 47·9; H, 4·3; N, 9·3; Cl, 11·8%). As it contained no water of crystallisation, it was evident that it was the hydrochloride of 6-aminodihydrocoumarincarbamylacetic acid. To isolate the free acid, the hydrochloride was dissolved in a small volume of cold water and very dilute aqueous sodium hydroxide added drop by drop till the solution was almost neutral. Colourless crystals (rectangular plates) slowly filled the liquid; they were washed with cold water and with alcohol: m. p. 170—171° (decomp.) (Found : C, 54·1; H, 4·9. $C_{12}H_{12}O_5N_2$ requires C, 54·5; H, 4·6%). The acid was insoluble in alcohol and was easily soluble in cold dilute acid or alkali and underwent decomposition when these solutions were warmed. When diazotised and coupled with β-naphthol, the hydrochloride as well as the free acid gave rise to scarlet-red azo-compounds.

I wish to thank Professor Robinson and Professor Dey for their continued interest in this work and for many helpful suggestions during its progress.

THE UNIVERSITIES OF MADRAS AND MANCHESTER. [*Received, October 28th, 1927.*]

XXV.—*The Formation of 2-Methylbenziminazoles.*

By MONTAGUE ALEXANDRA PHILLIPS.

THE nitration of diacetyl-*m*- and -*p*-phenylenediamine has been studied by Barbaglia (*Ber.*, 1874, **7**, 1258), Biedermann and Ledoux (*ibid.*, p. 1533), Ladenburg (*Ber.*, 1884, **17**, 150), and Bülow and

Mann (*Ber.*, 1897, **30**, 986), but the nitration of diacetyl-*o*-phenylenediamine does not appear to have been recorded hitherto. This nitration gives in good yield 4-nitrodiacetyl-*o*-phenylenediamine, the orientation of which was determined by reduction, followed by acetylation, 1 : 2 : 4-triacetamidobenzene being obtained identical with the products of reduction and subsequent acetylation of 4-nitrodiacetyl-*m*-phenylenediamine and 3-nitrodiacetyl-*p*-phenylenediamine.

4-Nitrodiacetyl-*o*-phenylenediamine was obtained by Ladenburg (*loc. cit.*) by the action of acetic anhydride on 4-nitro-*o*-phenylenediamine. Heim's suggestion (*Ber.*, 1888, **21**, 2307) that Ladenburg's compound was 5-nitro-2-methylbenziminazole is unfounded, since a repetition of Ladenburg's work gave 4-nitrodiacetyl-*o*-phenylenediamine identical with the product obtained as described above. The melting point recorded by Ladenburg (227°) is, however, low.

On reduction, 4-nitrodiacetyl-*o*-phenylenediamine gives an amino-compound which reacts normally with nitrous acid to give a diazo-compound, whereas the isomeric 4-aminodiacetyl-*m*-phenylenediamine and 3-aminodiacetyl-*p*-phenylenediamine both react with nitrous acid to give 5-acetamido-1 : 2 : 3-benztriazole, thus showing the equivalence of the 5- and the 6-position in the benztriazole system (compare Bülow and Mann, *loc. cit.*). On boiling mono- or di-acetyl-*o*-phenylenediamines with 3—4*N*-hydrochloric acid for several minutes, the corresponding 2-methylbenziminazoles are formed in good yield (compare Bistrzycki and Ulferrs, *Ber.*, 1892, **25**, 1992; Waljaschko and Boltina, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1780). The first stage of ring closure of diacetyl-*o*-phenylenediamine is hydrolysis to the monoacetyl compound, since *o*-aminoacetanilide has been isolated from the reaction mixture (compare Baxter and Fargher, J., 1919, **115**, 1373).

It appears, therefore, that hydrolysis of the diacetyl compound is favourable to rapid ring closure; this explains the difficulty of obtaining 2-methylbenziminazole from *o*-phenylenediamine by treatment with acetic anhydride (compare Ladenburg, *loc. cit.*; Heim, *loc. cit.*; Borsche and Rantscheff, *Annalen*, 1911, **379**, 150). 2-Methylbenziminazole was, however, obtained by boiling *o*-phenylenediamine with a mixture of acetic anhydride (0·5 g.-mol.) and 3—4*N*-hydrochloric acid: it is assumed that acetylation followed by ring closure occurred. Treatment of *o*-phenylenediamine with acetic anhydride (0·5 g.-mol.) gave a mixture of diacetyl-*o*-phenylenediamine and unchanged material; excess of acetic anhydride gave diacetyl-*o*-phenylenediamine only.

5-Amino-2-methylbenziminazole, isolated as the dihydrochloride or as the hydrochloride of the acetyl derivative, was formed by the

reduction of 5-nitro-2-methylbenziminazole and by the action of boiling 3*N*-hydrochloric acid on (i) 4-aminodiacetyl-*o*-phenylenediamine, (ii) 1 : 2 : 4-triacetamidobenzene, further de-acetylation having occurred, (iii) 4-aminodiacetyl-*m*-phenylenediamine and 3-aminodiacetyl-*p*-phenylenediamine. Case (iii) not only indicates the intermediate formation of these two bases in case (ii) but also confirms the work of Gallinek (*Ber.*, 1897, **30**, 1912) showing the identity of the 5- and the 6-position in the benziminazole system.

5-Acetamido-2-methylbenziminazole hydrochloride, m. p. 325°, has solubilities and a crystalline form similar to those of the compound, m. p. 324°, described without analytical data by Gallinek (*loc. cit.*) as the base. On treatment of its aqueous solution with ammonia, the base, m. p. 250°, separated (compare Kym, D.R.-P. 288190).

In similar experiments with 4-hydroxy- and 4-acetoxy-diacetyl-*o*-phenylenediamine, red amorphous solids but no benziminazole derivatives were isolated.

These reactions are being extended to derivatives of 3 : 4-diaminophenylarsinic acid.

EXPERIMENTAL.

o-Aminoacetanilide was obtained by adding a mixture of *o*-nitroacetanilide (180 g.) and iron powder (110 g.) to boiling water (1 l.) containing 50 c.c. of glacial acetic acid, a few drops of amyl alcohol being added from time to time to overcome the otherwise troublesome frothing. After being neutralised to litmus, filtered, and concentrated to small bulk, the solution deposited the amino-compound in 90% yield as white, hexagonal plates, m. p. 133° (Found: N, 18·7. Calc.: N, 18·7%).

Diacetyl-*o*-phenylenediamine was obtained by addition of acetic anhydride (200 c.c.) to the filtrate from the above reduction mixture. It separated as white, hexagonal prisms, m. p. 184°, and the yield, including material recovered from the mother-liquor, was 90% of the theoretical (Found: N, 14·6. Calc.: N, 14·6%).

Diacetyl-*m*-phenylenediamine and *diacetyl-p-phenylenediamine* were obtained in good yield from *m*-phenylenediamine hydrochloride and *p*-aminoacetanilide hydrochloride solutions respectively by treatment with sodium acetate and acetic anhydride in slight excess.

Nitration of the Three Diacetylphenylenediamines.—The compound (64 g.) was dissolved at 20° in sulphuric acid (240 c.c.) and nitrated at 5—10° with a mixture of nitric acid (*d* 1·42; 22 c.c.) and sulphuric acid (24 c.c.). When the product was poured into ice-water the nitro-compound was precipitated in 90% yield.

4-Nitrodiacetyl-*m*-phenylenediamine, m. p. 246°, formed white needles from 50% acetic acid (compare Barbaglia, *loc. cit.*), and

3-nitrodiacetyl-*p*-phenylenediamine, m. p. 185°, pale yellow needles from alcohol (compare Ladenburg, *loc. cit.*). 4-Nitrodiacetyl-*o*-phenylenediamine formed white or pale yellow prisms, m. p. 255°, from 50% acetic acid. It is sparingly soluble in hot water, more readily soluble in alcohol or hot glacial acetic acid (Found : N, 17·7. Calc. : N, 17·7%). It was also obtained by reducing 2 : 4-dinitroaniline with ammonium sulphide (compare Heim, *loc. cit.*) and boiling the resulting 4-nitro-*o*-phenylenediamine, m. p. 197—198°, with an excess of acetic anhydride; no trace of 5-nitro-2-methylbenziminazole was detected even after several hours' boiling.

Reduction of the Three Nitrodiacetylphenylenediamines.—The compound (44 g.) mixed with iron powder (88 g.) was reduced by the method described for the preparation of *o*-aminoacetanilide. The filtrate on concentration deposited the amino-compound, the total yield in each case (including material recovered from mother-liquors) being almost quantitative.

2-*Aminodiacetyl*-m-*phenylenediamine*, m. p. 250°, formed white prisms from water. It is moderately easily soluble in cold water and in alcohol (Found : N, 20·4. $C_{10}H_{13}O_2N_3$ requires N, 20·3%). 3-Aminodiacetyl-*p*-phenylenediamine, m. p. 231—232°, has been described by Bülow and Mann (*loc. cit.*). 4-*Aminodiacetyl*-o-*phenylenediamine*, m. p. 205°, forms white prisms from water. It resembles the above isomerides in solubility (Found : N, 20·1%). 1 : 2 : 4-Triacetamidobenzene, which crystallises from hot water in needles, m. p. 239°, was obtained by adding sodium acetate and acetic anhydride to an acid solution of any of the three amino-diacetylphenylenediamines and also by adding acetic anhydride to the filtrates obtained in the reduction of the nitrodiacetylphenylene-diamines. Concentration of the solutions was necessary to obtain good yields and the "mixed melting points" were undepressed (Found for specimens prepared by the six methods mentioned : N, 16·9, 16·8, 16·9, 16·8, 16·8, 16·8. Calc. : N, 16·9%).

Action of Nitrous Acid on 4-Aminodiacetyl-o-*phenylenediamine.*—This amine in the presence of 2—3 molecules of mineral acid gave a diazo-solution which reacted with sodium arsenite (Lewis and Cheetham, *J. Amer. Chem. Soc.*, 1921, **43**, 2119), 3 : 4-diacetamido-phenylarsinic acid being produced in good yield.

2-*Methylbenziminazole.*—(i) *o*-Phenylenediamine (1·1 g.), hydrochloric acid (15%; 10 c.c.), and acetic anhydride (1 c.c.) were boiled together under reflux for 20 minutes. On addition of sodium hydroxide solution until the mixture was faintly acid to litmus, 2-methylbenziminazole separated in 60% yield. It crystallised in white prisms, m. p. 176°, from hot water and was readily

soluble in mineral acids and in excess of caustic alkali (Found: N, 21·4. Calc.: N, 21·2%).

(ii) *o*-Aminoacetanilide (5 g.) or diacetyl-*o*-phenylenediamine (5 g.), on refluxing for 15 minutes with 10% hydrochloric acid (25 c.c.), gave in each case a 78% yield of the ring compound (*Found*: *N*, 21·4, 21·4%).

(iii) Diacetyl-*o*-phenylenediamine (1 g.), after boiling with 2—3*N*-hydrochloric acid (5 c.c.) for 1 minute, gave on neutralisation a mixture of prisms and hexagonal plates which, by fractional crystallisation from hot water, was shown to consist of *o*-amino-acetanilide (0·2 g.; m. p. 134°. Found: N, 18·8%) and 2-methyl-benziminazole (0·2 g.; m. p. 176°. Found: N, 21·2%).

(iv) Acetic anhydride (0·5 c.c.; $\frac{1}{2}$ mol.) was added to *o*-phenylene-diamine (1·1 g.). When vigorous reaction had ceased, the mixture was warmed in the water-bath for 1 minute. The solution on cooling deposited a mixture of diacetyl-*o*-phenylenediamine, m. p. 186°, and *o*-phenylenediamine, m. p. 102°, which was separated by fractionation from hot water, in which the latter is more soluble.

5-*Nitro*-2-*methylbenziminazole*.—(i) 4-Nitrodiacetyl-*o*-phenylene-diamine (47 g.) was boiled for not less than 1 hour with 25% sodium hydroxide solution (250 c.c.). On addition of hydrochloric acid until the precipitate first formed redissolved, and treatment of the filtered solution with sodium acetate until it was no longer acid to Congo-red, 5-nitro-2-methylbenziminazole was formed (20 g.; 55%).

Treatment for shorter periods with hot alkali causes the product to acquire a yellow colour which is difficult to remove.

(ii) 4-Nitrodiacetyl-*o*-phenylenediamine (11 g.), after refluxing for 15 minutes with hydrochloric acid (10%; 10 c.c.), gave, on addition of sodium acetate, 5-nitro-2-methylbenziminazole (6 g.; 80%), which was obtained quite white by repeated crystallisation from water. Treatment lasting only 1 to 3 minutes gave the same product, but it was sometimes accompanied by a small amount of 4-nitro-*o*-phenylenediamine, m. p. 199°.

5-Nitro-2-methylbenziminazole made by the above methods or by the methods of Heim (*loc. cit.*) and of Fischer and Hess (*Ber.*, 1903, **36**, 3970) consisted of white, staggered plates, m. p. 221°, readily soluble in hot water, mineral acids and caustic alkalis. It is unacted upon by nitrous acid, or by sulphuric acid at 90° (Found: N, 23·9. Calc.: N, 23·7%).

5-*Acetamido*-2-*methylbenziminazole*.—(i) Any one of the three aminodiacetylphenylenediamines described above (1 g.), after refluxing for 20 minutes with 4*N*-hydrochloric acid (10 c.c.), gave, on cooling, neutralisation, and addition of acetic anhydride (1 c.c.),

characteristic crystals of 5-acetamido-2-methylbenziminazole hydrochloride in 75% yield.

(*ii*) 1 : 2 : 4-Triacetamidobenzene (10 g.) was boiled under reflux for 30 minutes with 4*N*-hydrochloric acid (40 c.c.). The filtered solution on neutralisation to litmus and addition of acetic anhydride (10 c.c.) gave the above-mentioned hydrochloride in 80% yield.

(iii) 5-Nitro-2-methylbenziminazole (5 g.) mixed with iron powder (10 g.) was reduced by the general method described under *o*-aminoacetanilide. On addition of acetic anhydride (10 c.c.) to the filtrate from the neutralised reaction mixture 5-acetamido-2-methylbenziminazole separated.

The hydrochloride consists of stout, white, irregular, hexagonal plates, m. p. 325°, but is sometimes obtained as prismatic needles which rapidly change to the plates. It is sparingly soluble in cold water (Found: N, 18·4; Cl, 15·7. Calc.: N, 18·6; Cl, 15·7%). 5-Acetamido-2-methylbenziminazole is obtained by treatment of a warm aqueous solution of its hydrochloride with ammonia. It forms white prisms, m. p. 250°, is insoluble in cold water but readily soluble in mineral acids and in excess of caustic alkalis (Found: N, 22·2. Calc.: N, 22·2%). Treatment with concentrated hydrochloric acid gives the hydrochloride.

5-Amino-2-methylbenziminazole Dihydrochloride.—(i) 1 : 2 : 4-Triacetamidobenzene (40 g.) was treated as described under 5-acetamido-2-methylbenziminazole (ii). The filtered solution was evaporated to dryness under reduced pressure, and the residue crystallised from boiling concentrated hydrochloric acid, a 50% yield of the pure dihydrochloride being obtained.

(ii) 5-Acetamido-2-methylbenziminazole (2 g.) was heated under reflux for 1 hour with concentrated hydrochloric acid (4 c.c.). On cooling, 5-amino-2-methylbenziminazole dihydrochloride separated in white prisms, readily soluble in water (Found: N, 19·2; Cl, 32·6. Calc.: N, 19·1; Cl, 32·3%). The free base cannot readily be obtained owing to its solubility in water (compare Gallinek, *loc. cit.*).

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XXVI.—*Optical Activity and the Polarity of Substituent Groups. Part VII.* sec.-*β-Octyl Esters of* o-, m-, *and* p-*Substituted Benzoic Acids.*

By H. Gordon Rule, William Hay, Annie H. Numbers, and T. Ramsay Paterson.

In recent years a considerable amount of attention has been directed towards the influence of substituents on the physical and chemical behaviour of a parent compound. These researches have had to do with such diverse properties as benzene substitution, velocity of reaction, optical activity, dielectric constants, and physical state. As a result, it has been made abundantly clear that in nearly all these cases the main influence at work falls into one of two categories.

The first and most commonly observed influence is that usually described as the *general effect* of the substituent, which is regarded as being due to a general shift of the valency electrons away from an electropositive group such as CH_3, and towards an electronegative one such as NO_2, CO_2H, or Cl. This influence leads to a series of the following kind (I) representing a progressive change

NO_2, CO_2H, halogens, OMe, H,Me, . . . (I)

as we pass from NO_2 to Me. An excellent example of this type has been furnished by Olivier (*Rec. trav. chim.*, 1923, **42**, 516, 775) in the velocity of hydrolysis of substituted benzyl chlorides, for which the above sequence (omitting OMe) has been found to hold, irrespective of the position of the substituent in the nucleus. Apart from occasional minor deviations, the same order of the groups is repeated in their influence on the velocity of a number of other reactions, on the dissociation of acids, and on the dielectric constants of aromatic and aliphatic compounds (Rule and Paterson, J., 1924, **125**, 2155; Höjendahl, *Nature*, 1926, **117**, 896; Errera, *Compt. rend.*, 1926, **182**, 1623). In addition, the general effect of substituents has been traced in their influence on the optical activity of menthyl and *sec.*-β-octyl esters of monosubstituted acetic acids (Rule and Smith, J., 1925, **127**, 2188; Rule and Mitchell, J., 1926, 3202).

The group effect of the second type is represented by a series such as

(NH_3^+), NO_2, CO_2H,CH_3·CO,H, CH_3, I, Br, Cl, O·CH_3, (CO·O−) (II)

which indicates the relative influence of the substituents on the nitration of a monosubstituted benzene, and on the optical rotatory

powers of the menthyl esters of *o*-substituted benzoic acids. An effect of this type, however, is not peculiar to benzene compounds, as it is also exhibited in the rotatory powers of the *d*-amyl derivatives, $C_4H_9{\cdot}CH_2X$, and in certain chemical reactions in which those groups which are *m*-directive in benzene substitution produce an effect in the opposite sense to those which are *o,p*-directive (Henderson and Macbeth, J., 1922, **121**, 892; Hirst and Macbeth, *ibid.*, p. 904). The actual positions of the electrically charged ionic complexes $-NH_3^+$ and $\cdot CO{\cdot}O^-$ in this series are somewhat indefinite, but there appears to be no doubt that the former is to be ranged on the left hand side of hydrogen and the latter on the right (Rule, J., 1927, 54).

In connexion with the directive powers of these groups on the course of benzene substitution, it has been suggested that the differences are related to the residual valency of the substituent atom, leading in some cases to actual or incipient electron-sharing between it and the attached carbon atom (Robinson, *J. Soc. Chem. Ind.*, 1925, **44**, 456; Allan, Oxford, Robinson, and Smith, J., 1926, 401; Ingold and Ingold, *ibid.*, p. 1310).

The present communication deals with the optical rotatory powers of a number of *sec.*-β-octyl esters of *o*-, *m*-, and *p*-substituted benzoic acids. In Table I will be found a summary of the values of $[M]_D^{20°}$ obtained for the *o*-derivatives, together with those observed by Cohen (J., 1914, **105**, 1892) for the corresponding menthyl esters, and figures illustrating the influence of the substituents on benzene substitution. Table II records the rotatory powers of *sec.*-β-octyl esters of *m*- and *p*-substituted benzoic acids and the data referring to other properties mentioned above.

The rotatory power of *d*-β-octyl hydrogen phthalate in a number of solvents has already been determined by Pickard and Kenyon (J., 1907, **91**, 2058), who found, for example, $[M]_D^{20°} = +135{\cdot}2°$ in 5% alcoholic solution. The rotatory powers of this ester at different temperatures in the homogeneous state have now been measured for the purpose of discovering the sign of the temperature coefficient. The molecular rotation of the fused phthalate is $[M]_D = +91{\cdot}4°$ at 90·5°, and increases slowly with fall of temperature. This value is very much lower than that quoted above for 5% alcoholic solution, and determinations were therefore made of the rotatory powers in alcohol and acetone at concentrations up to the saturation points (see Table III) in the hope of deducing the rotation corresponding to the ester in the homogeneous supercooled state at 20°. Unfortunately, the solubility of the compound proved too low for this to be accomplished. It could only be concluded from the rotation curves that the value lies between + 95° and + 117° and probably

approximates to 95°. In a number of other solvents the solubility was very much lower than in alcohol and acetone.

TABLE I.

Molecular Rotatory Powers, $[M]_D^{20^\circ}$, *of Optically Active Esters of* o-*Substituted Benzoic Acids.*

Substit. X.	*l*-Octyl esters.	*l*-Menthyl esters.§	Nitration of C_6H_5X.‡ % *m*-.	% *p*-.
NO_2	−122°*	−381°	93	0·4
CO_2H	90—117	332	76	1·2
H	77·8 †	239	—	—
Me	68·1	231	3·1	41
I	44·3	237	—	66
Br	49·2	205	0·3	62
Cl	47·1	195	—	70
OMe	33·0 *	148	Chiefly *p*- and *o*-.	

TABLE II.

Molecular Rotatory Powers, $[M]_D^{20^\circ}$, *of* 1-*Octyl Esters of* m- *and* p-*Substituted Benzoic Acids.*

X.	*m*-Esters.	*p*-Esters.	Dissoc. consts. of acids. 1 : 2- $C_6H_4X{\cdot}CO_2H$.	$CH_2X{\cdot}CO_2H$.	Hydrolysis of 1 : 3- $C_6H_4X{\cdot}CH_2Cl$.
NO_2	−107·8°	—119·7°*	0·62	—	0·044
CO_2H ...	—	119·1	0·121	0·158	0·109
OMe	93·7	113·3*	—	0·033	—
Cl	92·4	103·6	0·13	0·155	0·137
Me	94·0	103·5	0·013	0·001	1·30
H	77·8	77·8	0·007	0·002	1·00

TABLE III.

Rotatory Powers of d-*Octyl Hydrogen Phthalate.*

Solvent.	G./100 c.c.	$[M]_D^{20^\circ}$.	Solvent.	G./100 c.c.	$[M]_D^{20^\circ}$.
Alcohol (20°)	5·000	+134·0°	Acetone (20°)	5·000	+121·0°
,,	20·000	131·5	,,	20·000	120·1
,,	30·000	129·5	,,	30·000	119·6
,,	36·800	128·6	,,	35·000	119·1
Homog. (90·5°)	—	91·4 ‖			

* Rule and Numbers, J., 1926, 2116.

† Pickard and Kenyon, J., 1915, **107**, 122.

‡ Holleman, "Die direkte Einführung von Substituenten," 1910, p. 199.

§ Cohen, *loc. cit.*

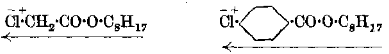
‖ This rotation increased slowly with fall of temperature. The recovered ester had a lower rotation than the initial material owing to the occurrence of slight decomposition in the fused state, hence it was not possible to obtain accurate values.

Influence of Substituents.—The values recorded in Table I show that ortho-substitution affects the rotatory power of *sec.*-β-octyl benzoate in precisely the same manner as it does that of menthyl benzoate. Substituents which are *m*-directive in type raise the nitration and those which are *o*, *p*-directive lower it. Further, the

relative influence of the various substituents on rotatory power goes hand in hand with their relative influence on benzene substitution. A partial exception to this statement is found in iodine, which undergoes a small displacement in each of the columns.

On the other hand, the molecular rotations recorded for the *m*- and *p*-substituted esters reveal an influence of a totally different character. Here the *general effect* of the groups is plainly visible, the agreement, as might be expected, being more definite in the *p*- than in the *m*-series. In the *sec.*-β-octyl benzoates, therefore, we have for the first time an example of a series of optically active compounds in which both types of effect (I and II) can be clearly demonstrated.

An increase in the rotatory power of the benzoate, following on *p*-substitution by NO_2,Cl, or a similarly oriented dipole grouping, might have been anticipated from a knowledge of the rotatory powers of the substituted acetic esters. In both cases the introduction of the dipole should result in a shift of the electrons away from the asymmetric atom and hence to similar changes in rotation.



A positively charged ionic complex should behave in the same manner. Nevertheless, the almost negligible change in the rotatory power of menthyl benzoate resulting from *m*- or *p*-substitution is a puzzling feature for which no adequate explanation can yet be advanced.

The general effect of a given group appears to vary somewhat with the compound and property under examination. In Table II, for instance, it is seen that the methyl group, instead of occupying its expected place below hydrogen in the series, at times falls in the position above it. Similarly, the relative positions of the three halogens among themselves are frequently found to undergo change. Variations of this kind are possibly due to a superimposed secondary influence resulting from molecular association. It is worthy of remark, however, that the general effect is a powerful one, and readily observed even when the substituent is several removes from the asymmetric carbon atom. The facility with which it is transmitted through long chains has already been commented upon by Robinson and Robinson (J., 1926, 2204) in connexion with the hydration of stearolic acid (compare also Olivier and Berger, *Rec. trav. chim.*, 1926, 45, 710). The influence of type II, on the contrary, appears to be a comparatively local one. It cannot be traced in the menthyl or octyl esters of substituted acetic acids although it is visible in the amyl derivatives, C_4H_9·CH_2X, where

the substituent is only separated from the asymmetric atom by a single methylene group.

Dispersion.—Although the dispersion of most, if not all, of the homogeneous esters is probably complex, it is found that the graphs for $1/\alpha$ against λ^2, over the range λ_{5893} to λ_{4358}, approximate very closely to straight lines. The *o*-bromo- and *o*-toluic esters were examined over the range λ_{6708} to λ_{4358}, and gave linear graphs. The *o*-nitro- and *o*-methoxy-derivatives (*loc. cit.*) show definitely complex dispersion.

Values of the dispersion ratio, $\alpha_{4358}/\alpha_{5893}$, vary from 2·04 to 2·17, with abnormal values for the *o*-nitro-ester in alcohol (2·698) and for the *o*-methoxy-ester (1·51). In all cases the dispersion ratios tend to rise with temperature.

Influence of Temperature.—With one partial exception, all the octyl esters of substituted benzoic acids so far examined are affected similarly by a rise in temperature, in that the influence of the substituent—whether resulting in a depression or in an exaltation of the rotatory power of the parent compound—becomes less pronounced.

In the case of the *o*-toluic ester, however, the temperature variations are very small. Values of $[M]_{6708}$ fall slightly with increasing temperature, and those of $[M]_{4358}$ rise somewhat. For this compound there appears to be a maximum rotatory power between 20° and 90°, which occurs at a higher and higher temperature as the wave-length diminishes.

EXPERIMENTAL.

The active *sec.*-β-octyl alcohol required for the following preparations was obtained by the method of Pickard and Kenyon as modified by Kenyon (J., 1922, **121**, 2540). It had a rotation of $\alpha_D^{15°} = \pm 8{\cdot}22°$ ($\pm 0{\cdot}04°$) in a 1-dcm. tube.

Special care was taken to ensure the purity of the initial materials. In the majority of cases the acids, as purchased or prepared, were purified by repeated crystallisation. Terephthalic acid was obtained from redistilled diethyl terephthalate by hydrolysis. Acid chlorides were prepared by means of purified thionyl chloride and were fractionated before use.

Unless otherwise stated, all the following esters were obtained in the form of colourless, odourless liquids.

d-β-*Octyl Hydrogen Terephthalate.*—Terephthalic acid was converted into the diacid chloride by treatment with phosphorus pentachloride and the acid chloride was recrystallised from benzene until pure, m. p. 75—78°.

Terephthalyl chloride (21 g.) was mixed with *d*-β-octyl alcohol

(26 g.) and pyridine (32 g.), and heated under reflux for 4 hours at 120°. The *di-ester, which cannot be distilled without decomposition,* was separated in the usual way; yield, 33—34 g. of crude product.

Earlier attempts to carry out the half hydrolysis of dioctyl terephthalate in methyl or ethyl alcoholic solution, with or without the addition of water, resulted only in the formation of methyl or ethyl hydrogen terephthalate. The crude ester (33 g.) was therefore made into an emulsion with a solution of potassium hydroxide (5·1 g.) in water (5 c.c.) and pure *d*-β-octyl alcohol (43 g.). After 2 days, the thick, creamy mixture was heated on the water-bath till nearly neutral. The product was diluted with water and any free alcohol and unchanged ester were extracted with ether. The aqueous solution was made acid and the precipitated octyl hydrogen terephthalate removed in ether. The washed and dried ethereal solution gave on distillation of the solvent 17 g. of crude ester, which readily solidified. After crystallisation from ligroin, it melted at 95—96° and had $[\alpha]_D^{19°} = +45·17°$ in acetone ($l = 2$, $c = 5·004$). The rotatory power was not changed by three further recrystallisations. d-β-*Octyl hydrogen terephthalate* crystallises in large, transparent plates. It is readily soluble in ligroin and even more soluble in acetone (Found: C, 69·0; H, 8·2. $C_{16}H_{22}O_4$ requires C, 69·0; H, 8·0%).

d-β-*Octyl* o-*chlorobenzoate* was prepared in the usual way from *o*-chlorobenzoyl chloride (12 g.), *d*-β-octyl alcohol (9 g.), and pyridine (12 g.). Yield 16·0 g.; b. p. 180°/14 mm. The rotatory power did not change on further fractionation (Found: Cl, 13·4. $C_{15}H_{21}O_2Cl$ requires Cl, 13·2%). d-β-*Octyl* m-*chlorobenzoate* from *m*-chlorobenzoyl chloride is a liquid, b. p. 175°/12 mm. (Found: Cl, 13·3%). d-β-*Octyl* p-*chlorobenzoate* from *p*-chlorobenzoyl chloride boils at 177—178°/12 mm. (Found: Cl, 13·5%). d-β-*Octyl* o-*bromobenzoate* from *o*-bromobenzoic acid (m. p. 148·5—149°) is a colourless liquid, b. p. 175°/9 mm. (Found: Br, 25·3. $C_{15}H_{21}O_2Br$ requires Br, 25·5%). d-β-*Octyl* o-*iodobenzoate* from *o*-iodobenzoic acid (m. p. 162·5—163°) was obtained as a liquid, b. p. 202°/12 mm., which was coloured yellow owing to a trace of free iodine (Found: I, 35·3. $C_{15}H_{21}O_2I$ requires I, 35·25%).

d-β-*Octyl* o-*toluate* from *o*-toluic acid boiled at 154—155°/9 mm. (Found: C, 77·4; H, 10·0. $C_{16}H_{24}O_2$ requires C, 77·3; H, 9·75%). d-β-*Octyl* m-*toluate* from *m*-toluic acid boiled at 181·5—182°/17 mm. (Found: C, 77·3; H, 9·9%). d-β-*Octyl* p-*toluate* from *p*-toluic acid boiled at 184°/19 mm. (Found: C, 77·25; H, 9·9%).

Observed Densities and Rotations of the Homogeneous Esters.—The following rotations of the homogeneous esters were determined in a 1-dcm. tube, except in a few cases (marked *) where one of 0·5-dcm.

was employed. Densities were measured at four temperatures between 20° and 95°, in a pyknometer holding 3—5 c.c.

All rotations are of the same sign as that of the alcohol from which the esters are derived.

d-β-Octyl *o*-chlorobenzoate ($l = 1$).

$D_{4^\circ}^{t^\circ}$ 1·0473 at 20°; 1·0319 at 39·0°; 1·0134 at 63°; 0·9960 at 85·0°.

α_{5893} 18·36° at 19·7°; 18·50° at 36·3°; 18·64° at 56·0°; 18·75° at 92·1°.

α_{5780} 19·17° at 19·8°; 19·27° at 36·3°; 19·64° at 55·3°; 19·54° at 95·3°.

α_{5461} 21·79° at 19·7°; 21·98° at 36·3°; 22·22° at 55·6°; 22·31° at 95·3°.

α_{4358} 36·90° at 19·8°; 37·52° at 36·3°; 38·20° at 55·3°; 38·85° at 95·6°.

d-β-Octyl *m*-chlorobenzoate ($l = 1$).

$D_{4^\circ}^{t^\circ}$ 1·0425 at 20°; 1·0272 at 39°; 1·0087 at 63°; 0·9912 at 85°.

α_{5893} 35·87° at 20·0°; 34·89° at 35·0°; 33·39° at 61·2°; 31·87° at 94·3°.

α_{5780} 37·51° at 20·0°; 36·47° at 35·0°; 34·98° at 61·2°; 33·26° at 94·3°.

α_{5461} 42·74° at 20·0°; 41·53° at 35·0°; 39·87° at 61·2°; 37·88° at 94·3°.

α_{4358} 73·74° at 20·0°; 71·71° at 35·0°; 68·93° at 61·2°; 65·67° at 94·3°.

l-β-Octyl *p*-chlorobenzoate ($l = 1$).

$D_{4^\circ}^{t^\circ}$ 1·0403 at 20·7°; 1·0257 at 39°; 1·0074 at 63°; 0·9902 at 85°.

α_{5893} 40·10° at 20·5°; 38·90° at 37·0°; 37·58° at 55·8°; 35·21° at 95·3°.

α_{5780} 42·02° at 20·5°; 40·72° at 37·0°; 39·33° at 55·8°; 36·66° at 95·3°.

α_{5461} 47·94° at 20·5°; 46·56° at 37·0°; 44·98° at 55·8°; 41·96° at 95·3°.

α_{4358} 83·96° at 20·5°; 81·44° at 37·0°; 78·86° at 55·8°; 73·75° at 95·3°.

d-β-Octyl hydrogen phthalate.

$D_{4^\circ}^{t^\circ}$ 1·027 at 72°; 1·022 at 80·6°; 1·016 at 90·5°; 1·015 at 92·5°

Rotations at 90·5° in 1-dcm. tube: $\alpha_{5893} = 33·40°$; $\alpha_{5780} = 35·02°$; $\alpha_{5461} = 40·46°$. The rotation of the fused acid falls slowly owing to decomposition. A re-examination of the same specimen gave $\alpha_{5461}^{92·5°} = 39·52°$; $\alpha_{5461}^{80·6°} = 39·99°$; $\alpha_{5461}^{72°} = 40·55°$.

d-β-Octyl *o*-bromobenzoate.

$D_{4^\circ}^{t^\circ}$ 1·1987 at 24·6°; 1·1764 at 48·8°; 1·1623 at 64·1°; 1·1435 at 84·6°.

α_{6708} 14·09° at 21·0°; 14·23° at 38·6°; 14·34° at 65·2°; 14·32° at 89·5°.

α_{5893} 18·89° at 21·0°; 19·07° at 38·6°; 19·18° at 65·2°; 19·17° at 89·5°.

α_{5870} 19·66° at 21·0°; 19·88° at 38·6°; 20·00° at 65·2°; 20·02° at 89·5°.

α_{5461} 22·53° at 21·0°; 22·73° at 38·6°; 22·92° at 65·2°; 22·93° at 89·5°.

α_{4358} 39·23° at 21·0°; 39·74° at 38·6°; 40·33° at 65·2°; 40·47° at 89·5°.

d-β-Octyl *o*-iodobenzoate.

$D_{4^\circ}^{t^\circ}$ 1·3522 at 18·9°; 1·3239 at 47·35°; 1·3131 at 58·3°; 1·2904 at 81·4°.

α_{6708} 12·33° at 18·3°; 12·74° at 40·4°; 13·03° at 60·5°; 13·33° at 89·0°.

α_{5893} 16·57° at 18·3°; 17·20° at 40·4°; 17·58° at 60·5°; 17·58° at 89·0°.

α_{5780} 17·33° at 18·3°; 17·95° at 40·4°; 18·38° at 60·5°; 18·70° at 89·0°.

α_{5461} 19·87° at 18·3°; 20·64° at 40·4°; 21·10° at 60·5°; 21·54° at 89·0°.

α_{4358} Rotations could not be taken owing to the yellow colour of the ester.

d-β-Octyl *o*-toluate.

$D_{4^\circ}^{t^\circ}$ 0·9522 at 22·6°; 0·9345 at 45·6°; 0·9250 at 58·1°; 0·9073 at 80·9°.

α_{6708} 19·64° at 20·0°; 19·31° at 39·2°; 18·71° at 70·2°; 9·16°* at 90·3°.

α_{5893} 26·18° at 20·0°; 25·78° at 39·2°; 25·00° at 70·2°; 12·25°* at 90·3°.

α_{5780} 27·32° at 20·0°; 26·88° at 39·2°; 26·10° at 70·2°; 12·77°* at 90·3°.

α_{5461} 31·10° at 20·0°; 30·64° at 39·2°; 29·79° at 70·2°; 14·615°* at 90·3°.

α_{4358} 53·36° at 20·0°; 52·78° at 39·2°; 51·64° at 70·2°; 25·42°* at 90·3°.

l-β-Octyl *m*-toluate.

$D^{t°}_{4°}$ 0·9492 at 20°; 0·9245 at 52·9°; 0·8997 at 84·7°.

α_{5893} 36·09° at 17·6°; 34·38° at 48·2°; 33·31° at 66·0°; 32·94° at 74·6°; 15·91°* at 98·2°.

α_{5780} 37·72° at 17·6°; 36·18° at 43·2°; 34·82° at 66·0°; 34·41° at 74·6°; 16·64°* at 98·2°.

α_{5461} 43·04° at 17·6°; 41·36° at 43·2°; 39·74° at 66·0°; 39·32° at 74·0°; 18·96°* at 98·2°.

α_{4358} 74·97° at 17·6°; 71·89° at 43·2°; 69·20° at 66·0°; 68·72° at 73·5°; 33·10°* at 98·2°.

l-β-Octyl *p*-toluate.

$D^{t°}_{4°}$ 0·9492 at 20°; 0·9264 at 49·5°; 0·9025 at 80·3°.

α_{5893} 39·45° at 22·2°; 38·65° at 36·6°; 37·77° at 52·4°; 17·65°* at 98·7°.

α_{5780} 41·29° at 22·0°; 40·45° at 36·6°; 39·26° at 57·2°; 18·45°* at 98·7°.

α_{5461} 47·25° at 21·8°; 46·30° at 36·6°; 45·40° at 52·4°; 21·06°* at 98·7°.

α_{4358} 82·50° at 21·8°; 81·14° at 35·4°; 79·46° at 52·4°; 37·15°* at 98·7°.

Dispersion Ratios of the Homogeneous Esters.

	d-β-Octyl *o*-chloro-benzoate.		*d*-β-Octyl *m*-chloro-benzoate.		*l*-β-Octyl *p*-chloro-benzoate.		*d*-β-Octyl *o*-bromo-benzoate.	
t.	$D^{t°}_{4°}$.	$\alpha_{4358}/\alpha_{5893}$.	$D^{t°}_{4°}$.	$\alpha_{4358}/\alpha_{5893}$.	$D^{t°}_{4°}$.	$\alpha_{4358}/\alpha_{5893}$.	$D^{t°}_{4°}$.	$\alpha_{4358}/\alpha_{5893}$.
20°	1·0473	2·010	1·0425	2·055	1·0411	2·092	1·2029	2·076
40	1·0313	2·029	1·0267	2·059	1·0252	2·098	1·1845	2·084
60	1·0156	2·043	1·0111	2·064	1·0097	2·098	1·1661	2·098
80	0·9997	2·061	0·9954	2·064	0·9941	2·097	1·1477	2·109
90	0·9918	2·067	0·9914	2·062	0·9903	2·096	1·1385	2·112
	l-β-Octyl *o*-toluate.		*d*-β-Octyl *m*-toluate.		*l*-β-Octyl *p*-toluate.		*d*-β-Octyl *o*-iodobenzoate.	
20	0·9542	2·038	0·9492	2·077	0·9492	2·089	1·3511	1·200†
40	0·9388	2·047	0·9339	2·076	0·9337	2·097	1·3313	1·200†
60	0·9235	2·059	0·9187	2·078	0·9182	2·104	1·3115	1·200†
80	0·9080	2·069	0·9035	2·080	0·9028	2·108	1·2918	1·203†
90	0·9003	2·074	0·8959	2·080	0·8951	2·110	1·2819	1·207†

† $\alpha_{5461}/\alpha_{5893}$.

Rotatory Powers of *d*-β-Octyl Hydrogen Terephthalate in Solution.

t.	Solvent.	*G.*/100 c.c.	$[M]_{5893}$.	$[M]_{5780}$.	$[M]_{5461}$.	$[M]_{4358}$.	$\alpha_{4358}/\alpha_{5893}$.
20°	Acetone	5·004	125·5°	132·5°	149·2°	265·6°	2·12
18·3	Benzene	4·304	119·0	125·3	142·1	258·6	2·17
18·0	Alcohol	5·020	119·1	126·4	145·2	253·0	2·12

Summary.

The rotatory powers of a number of octyl esters of *o*-, *m*-, and *p*-substituted benzoic acids have been determined in the homogeneous state, with the following results.

1. The relative influence of *o*-substituents is given by $NO_2 >$ $CO_2H > H > Me > Br > Cl > I > OMe$. Except for a small displacement of I, this series also represents the influence of the substituents on the rotatory power of menthyl benzoate and on benzene substitution.

2. In the *m*- and *p*-*positions* the influence of the substituents *accords closely* with their *general effect*, *e.g.*, for the *p*-series $NO_2 > CO_2H > OMe > Cl > CH_3 > H$. The electron-shift theory of the general effect being assumed, the change of rotation is in the direction anticipated from a knowledge of the rotatory powers of the substituted acetic esters.

The authors desire to express their indebtedness to the Earl of Moray Fund for a grant which has covered most of the expense incurred during this research.

EDINBURGH UNIVERSITY. [*Received, November 7th*, 1927.]

XXVII.—*Applications of Thallium Compounds in Organic Chemistry. Part IV. Thallium Compounds of Polyhydroxy-compounds.*

By ROBERT CHARLES MENZIES and MARGARET ELIZABETH KIESER.

IN Part I (Menzies and Wilkins, J., 1924, **125**, 1151), the qualitative reactions of thallous hydroxide with the sugars were described and it was shown that colour changes took place on heating, which were marked in the cases of glucose and fructose, the metal being reduced as a mirror under suitable conditions.

On boiling sucrose and mannitol, however, with 10% thallous hydroxide solution a faint yellow colour alone appears.

The precipitates formed in the cold when concentrated aqueous solutions of fructose, glucose, and galactose are mixed with a solution of thallous hydroxide give indefinite analytical figures, but definite compounds are formed by methylglucoside, and methylarabinoside, in which the reducing group is masked, and also by *thallous gluconate* and by sorbitol, from which it is absent. As a useful criterion of the purity of these compounds is a comparison of the total thallium content estimated by precipitation as iodide or as chromate with that estimated by titration, it is recalled that thallium replacing hydrogen in non-acidic hydroxyl groups is hydrolysed by water and may be estimated by titration with acid, 1 c.c. of *N*-acid indicating 0·2044 g. of the metal (see Part II, J., 1925, **127**, 2372).

The hydrolysis of thallous ethoxide, thallous phenoxide, and *trithallium methylarabinoside*, for instance, is so complete that estimations of the metal by titration and by precipitation give the same percentage figure. The normal thallous salts of acids, such as thallous tartrate, are not hydrolysed by water, the aqueous

solutions have a neutral reaction, and none of the thallium is estimable by titration. In hydroxy-acids in which thallium has replaced the hydrogen of both carboxyl and hydroxyl groups, that replacing the latter only is hydrolysed by water, so that part only of the metal is estimated by titration; *e.g.*, the thallium estimated by titration of tetrathallium tartrate, $C_2H_2(OTl)_2(CO_2Tl)_2$ (Part II), is half that estimated by precipitation as iodide, and titration of *hexathallium gluconate*, $C_5H_6(OTl)_5(CO_2Tl)$, indicates five-sixths of the total thallium, which may be estimated by precipitation. The formation of acid oxidation or decomposition products may lead to the contamination of the compounds with the thallium salts of these acids and thus depress the titration value, the total thallium content not being changed to the same extent, so that determinations of both values are necessary for the characterisation of the pure compounds.

The most marked example of this contamination yet encountered is afforded by a precipitate, obtained by treating fructose with 3·5 equivalents of thallous hydroxide [$C_6H_9O_3(OTl)_3$, $C_6H_8O_2(OTl)_4$, and $C_6H_7O(OTl)_5$ require Tl, 77·6, 82·3, and 85·4%, respectively], which gave 79·2% of metal as iodide but 54·9% by titration, indicating that acid products had been formed by oxidation of the fructose in amount sufficient to neutralise rather less than one-third of the thallous hydroxide formed by hydrolysis. Treatment of solutions of glucose and galactose in the cold with six equivalents of aqueous thallous hydroxide gave precipitates which showed high analytical figures—from glucose, Tl, 83·8, 83·5% by precipitation, 76·0, 77·1% by titration: from galactose, Tl, 81·6% by precipitation, 76·4% by titration—but here again the divergence is evidence of decomposition, and none of the three precipitates can be regarded as a well-defined compound, the combined action of the easily reducible metal and of atmospheric oxygen (not excluded in any of the experiments described) attacking the sugars in the alkaline solution even in the cold.

A closer approximation to a definite composition is shown by *trithallium methylglucoside*, the thallium estimated by precipitation being in good agreement with that required by the formula $C_7H_{11}O_3(OTl)_3$ (Fear and Menzies, J., 1926, 937). The thallium estimated by titration, however, is always less than that found by precipitation, the difference increasing the longer the aqueous solutions of the samples have been boiled; *e.g.*, a specimen which was filtered off shortly after the hot solutions of methylglucoside and thallous hydroxide were mixed gave Tl 76·4% by precipitation and 73·4% by titration, whereas a second crop, indistinguishable from the first in appearance, obtained by concentrating the mother-

liquor to half its bulk by boiling, gave corresponding values of 76·15 and 69·2% (the above formula requires Tl, 76·2%). For specimens rapidly prepared, titration values exceeding 75% have been obtained.

Methylarabinoside, which resembles methylglucoside in containing three secondary alcoholic groups but differs from it in containing no primary alcoholic group (Hirst, J., 1925, **127**, 358), also forms a trithallium derivative, the precipitation and titration values of which are in close agreement (Found: Tl, by precipitation 78·7, by titration 78·8. $C_6H_9O_5Tl_3$ requires Tl, 79·2%). In a second crop, obtained from the mother-liquor concentrated to small bulk by boiling, the thallium found by precipitation was 79%, and by titration, 78·1%. A solution of trithallium methylarabinoside, however, which had been boiled and allowed to cool slowly, gave on titration Tl 74·2%, suggesting that the greater ease with which this substance can be obtained pure may be due to the greater solubility of the impurity formed on heating. The non-substitution of one of the four hydroxylic hydrogen atoms of methylglucoside may be connected with the lack of activity of one of the hydroxyl groups of glucose to which attention has been directed by Schlubach and Firgau (*Ber.*, 1926, **59**, 2100), but a complete explanation cannot yet be attempted, as both gluconic acid and sorbitol form thallium derivatives in which all six available hydrogens are replaced by thallium, whereas solutions of sucrose mixed with thallous hydroxide in widely differing molecular proportions deposit tetrathallium sucrose, which it is hoped to describe in a future communication.

EXPERIMENTAL.

The two crops of *trithallium methylarabinoside*, details of the analyses of which have been given above, weighed together 1·14 g. and were prepared from 0·8 g. of α-methylarabinoside (kindly presented by Dr. A. K. Macbeth) and slightly more than 3 equivs. of thallous hydroxide, made by boiling 3·85 g. of thallous ethoxide (theoretical quantity for 3 equivs., 3·75 g.) with water until much hydroxide separated on cooling. The substance is exceedingly soluble in water, the first crop being obtained by concentrating the solution to small bulk by boiling, and the second from the mother-liquor in the same way. Both crops were filtered off with suction, washed with a little water, and dried on a porous plate over phosphoric anhydride. They darkened at 160°, became black between 200° and 210°, and melted and frothed at 215—220°.

When the mother-liquor was evaporated to dryness in a desiccator, yellow scales (0·77 g.) were formed which did not adhere to the bottom of the dish (Found by titration: Tl, 72·6%). There was

also a very small amount of a substance which adhered firmly to the bottom of the dish in rounded aggregates; these appeared white in reflected light, yellowish-brown in transmitted light, and as red circles with dark crosses in polarised light between crossed Nicols.

When 4 equivalents of thallous ethoxide were used, a first crop of 1·3 g. was obtained (Found: Tl, 78·8 as iodide; 78·0 by titration. Calc.: Tl, 79·2%). The second crop obtained by boiling was very small in amount, a colourless, transparent jelly being also formed. Trithallium methylarabinoside is unaltered by daylight.

Thallous Gluconate.—The preparation of crystalline *thallous gluconate* was delayed for 3 years owing to inability to obtain a nucleus. Treatment of a well-crystallised sample of mercury gluconate (Heffer, *Ber.*, 1889, **22**, 1049) with metallic thallium and water until the solution was free from mercury, and subsequent evaporation, gave a syrup which, after being flooded with methyl alcohol, crystallised over-night and then served to nucleate larger-scale preparations. By double decomposition of 11·2 g. of barium gluconate with a slight excess of thallous sulphate 10·5 g. of crude thallous gluconate (yield, 68%) were obtained. Several preparations of gluconic acid, each made from 50 g. of glucose by oxidation with bromine in the usual way, gave yields of 20—25 g. of thallous gluconate on neutralisation with thallous hydroxide solution, followed by evaporation to small bulk, nucleation, and subsequent recrystallisation.

Thallous gluconate is very soluble in water, a saturated solution forming a heavy viscous syrup from which rosettes of prisms crystallise slowly on nucleation. A sample prepared from barium gluconate and thallous sulphate had $[\alpha]_D + 3·3°$ in water ($c =$ 4·24%). It darkened at 134° and melted at 134—144° to a clear brown liquid (Found: Tl, 50·8, 51·2. $C_6H_{11}O_7Tl$ requires Tl, 51·2%). A sample prepared from gluconic acid and thallous hydroxide had $[\alpha]_D + 4·4°$ in water ($c = 3·9\%$). It darkened at 136° and melted at 133—138° to a very dark liquid (Found: Tl, 50·3, 50·6%). Thallous gluconate crystallises without water of crystallisation: a sample left over-night over phosphoric anhydride lost no further weight at 100°.

Hexathallium Gluconate.—Thallous gluconate (22 g.) in 80 c.c. of water was heated with a thallous hydroxide solution prepared by boiling 66 g. of thallous ethoxide (theoretical quantity for 5 equivs., 68·7 g.) with 100 c.c. of water until the alcohol formed was expelled; 44·3 g. of crude *hexathallium gluconate* were obtained as a yellow powder [Found: Tl, 85·2 by precipitation, 70·6 by titration. $C_5H_6(OTl)_5{\cdot}CO_2Tl$ requires Tl, 86·6% by precipitation, 72·2% by titration]. After some weeks the crude compound, which was

superficially darkened by light, was washed with a little hot water, filtered off with suction, and again dried to constant weight (Found by precipitation: Tl, 85·3, 85·35%. Found by titration, the standard acid being run directly on to the dried solid: Tl, 70·9, 69·8%. Found by titration in three separate experiments in which the salt had previously been dissolved in warm water: Tl, 65·75, 66·7, and 68%). A solution of the salt which had been boiled and allowed to stand for ½ hour gave Tl 65·6% on titration, and a sample which had been heated dry at 100° for 1 hour gave Tl 63·1%.

Theoretical figures, however, were obtained for a sample made from 4 g. of thallous gluconate and 12·3 g. of thallous ethoxide treated with water as before, and analysed immediately after it had dried to constant weight (Found: Tl, 86·6% by precipitation, 72·1% by titration).

Aqueous solutions of hexathallium gluconate are lævorotatory.

Thallium Compound of Sorbitol.—12·25 G. of the crude compound were obtained from 2 g. of sorbitol and an aqueous solution of thallous hydroxide made by treating 18 g. (6½ equivs.) of thallous ethoxide with water [Found: Tl, 86·6 by precipitation, 84·4 by titration. $C_6H_8(OTl)_6$ requires Tl, 87·5%]. After being washed with 15 c.c. of hot water, filtered off with suction, and again dried to constant weight, the substance gave Tl 86·8% by precipitation and 86·4% by titration. A sample which had been kept for 6 months gave Tl 80·7% on titration. The compound is superficially darkened by daylight.

9·4 G. of the compound were obtained in a second preparation from 2 g. of sorbitol and thallous hydroxide prepared from 12·4 g. of thallous ethoxide (4½ equivs.) (Found: Tl, 86·4% by precipitation, 87·9, 87·4% by titration). After being washed with water and treated as described above, the substance gave Tl 86·9% by precipitation and 87·7% by titration.

The first of the above washings contained 9·6 g. of dissolved solid in 100 c.c., was faintly dextrorotatory, and gave strikingly different figures on analysis by the two methods (Found: Tl 78·3% by precipitation, 57·5% by titration).

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THE UNIVERSITY, BRISTOL. [*Received, November 10th*, 1927.]

XXVIII.—*Studies in Adjacent Substitution. Part I. Some Reactions of 3-Chloro-2-aminoanisole.*

By Herbert Henry Hodgson and Arnold Kershaw.

Reactions already described of 3-halogeno-2-nitrophenols (Hodgson and Moore, J., 1925, **127**, 2260; 1926, 155; 1927, 1141) and 3-chloro-2-nitroanisole (Hodgson and Handley, J., 1926, 542) showed peculiarities which were tentatively ascribed to adjacent substitution. The results of the present investigation support that supposition.

3-*Chloro*-2-*aminoanisole* forms stable salts with hydrochloric, hydrobromic, and nitric acids (compare the stable hydrates of 3-chloro-2-nitrophenol, *loc. cit.*) and the sulphate, in marked contrast to aniline sulphate, is very soluble in water. The diazonium salts are stable even in boiling aqueous hydrochloric or sulphuric acid over a wide range of concentrations (compare Meldola, Woolcott, and Wray, J., 1896, **69**, 1327) and replacement of the diazo-group by hydroxyl has not yet been effected. Its replacement by halogens and cyanogen, however, takes place normally in the Sandmeyer reaction. 3-*Chloro*-2-*cyanoanisole* cannot be hydrolysed to the acid by the usual methods.

The colours of the hydrazones formed from 3-chloroanisyl-2-hydrazine and *o*-, *m*-, and *p*-nitrobenzaldehydes and the colours developed by products in alcoholic alkali are very similar to those given by the respective *o*-, *m*-, and *p*-nitrobenzaldehyde-2-chlorophenylhydrazones (Chattaway and Clemo, J., 1923, **123**, 3041).

The dyes formed by coupling diazotised 2-chloro-3-aminoanisole with Schäffer, R-, and N.W. salts give on wool colours which are more reddish-orange than those given by the corresponding unsubstituted aniline azo-dyes and exhibit the powerful hypsochromic effect of chlorine in the *o*-position with respect to the azo-group (compare Hodgson and Handley, this vol., p. 165). The differences in shade between the scarlet-red colours produced by the corresponding *o*-anisidine azo-dyes and the reddish-orange colours mentioned above are much greater than the differences in the case of the azo-dyes formed from aniline and from *o*-chloroaniline, the bathochromic effect of the methoxy-group being almost completely inhibited in the presence of the *o*-substituted chlorine.

Experimental.

3-*Chloro*-2-*aminoanisole*.—Iron powder (20 g.) was slowly added to a mixture of 50% acetic acid (140 g.) and 3-chloro-2-nitroanisole (30 g.) on the water-bath. After the vigorous reaction had abated, the mixture was heated for 1 hour and made slightly alkaline with sodium hydroxide solution, and 3-*chloro*-2-*amino*-

anisole was then obtained by steam-distillation in excellent yield as a colourless oil, b. p. 246° (slight decomp.) (Found: Cl, 22·4. C_7H_8ONCl requires Cl, 22·5%). It has a pleasant odour and is almost insoluble in water. It gives a brown coloration with bleaching powder after a few minutes, and a dark brown precipitate with bromine water. The carbylamine reaction only takes place with difficulty. The *hydrochloride* crystallises from water, in which it is only sparingly soluble, in long, colourless needles, m. p. 211° (Found: Cl, 36·5. C_7H_8ONCl,HCl requires Cl, 36·6%), the *hydrobromide* in colourless needles which sublime at 250° (0·0932 g. gave 0·1313 g. of silver halides. Calc.: 0·1296 g.), and the *nitrate*, which is much more soluble, in colourless needles, m. p. 137° (Found: Cl, 16·3. C_7H_8ONCl,HNO_3 requires Cl, 16·1%). The *monoacetyl* derivative, prepared from the amine (2 g.) and acetic anhydride (2·5 g.) on the water-bath, crystallises from 60% alcohol in colourless prisms, m. p. 123° (Found: Cl, 17·5. $C_9H_{10}O_2NCl$ requires Cl, 17·8%). The *diacetyl* derivative, formed by heating the amine with excess of acetyl chloride in glacial acetic acid, crystallises from dilute acetic acid in large, colourless plates, m. p. 145·5° (Found: Cl, 15·0. $C_{11}H_{12}O_3NCl$ requires Cl, 14·7%). The *benzoyl* derivative separates from alcohol in fine, colourless needles, m. p. 135° (Found: Cl, 13·9. $C_{14}H_{12}O_2NCl$ requires Cl, 13·6%).

2 : 3-Dichloroanisole, long, colourless plates, m. p. 33°, from alcohol (Holleman, *Rec. trav. chim.*, 1917, **37**, 96, gives m. p. 31°) (Found: Cl, 39·9. Calc.: Cl, 40·1%), 3-*chloro-2-bromoanisole*, long, colourless plates, m. p. 50° (0·1549 g. gave 0·2308 g. of silver halides. Calc.: 0·2318 g.), 3-*chloro-2-iodoanisole*, colourless, crystalline clusters, m. p. 53·5° (0·0999 g. gave 0·1424 g. of silver halides. Calc.: 0·1408 g.), and 3-*chloro-2-cyanoanisole*, fine, colourless needles, m. p. 114·5°, slowly volatile in steam (Found: Cl, 21·0. C_8H_6ONCl requires Cl, 21·2%), were all obtained in excellent yield by the Sandmeyer method.

3-*Chloro-2-thiocyanoanisole* forms colourless needles, m. p. 43° (Found: Cl, 17·9. C_8H_6ONClS requires Cl, 17·8%), volatile in steam.

3-*Chloroanisole-2-diazoperbromide* was obtained in bright orange micro-needles, m. p. 115—116° (decomp.), when a slight excess of bromine, dissolved in aqueous potassium bromide, was added to an aqueous solution of 3-chloroanisole-2-diazonium sulphate (0·0726 g. gave 0·1274 g. of silver halides. Calc.: 0·1254 g.). When boiled with glacial acetic acid, it gave 3-*chloro*-2 : 6-*dibromoanisole*, which crystallised from dilute acetic acid or alcohol in fine, colourless needles, m. p. 92° (0·0526 g. gave 0·0920 g. of silver halides. Calc.: 0·0906 g.) and was identified by comparison with a specimen obtained by the sulphonation of *m*-chlorophenol (the *p*-sulphonic acid

produced was identified in the form of potassium 3-chloro-6-nitrophenol-4-sulphonate), dibromination, desulphonation, and methylation.

3-Chloroanisole-2-diazoimide, obtained by the action of ammonia on the diazoperbromide, was volatile in steam and crystallised from light petroleum in pale yellow prisms, m. p. 35° (Found: Cl, 19·4. $C_7H_6ON_3Cl$ requires Cl, 19·3%).

3-Chloroanisyl-2-hydrazine hydrochloride, prepared by the reduction of 3-chloroanisole-2-diazonium chloride with stannous chloride in concentrated hydrochloric acid solution, crystallised from water in colourless needles (Found: Cl, 34·1. $C_7H_9ON_2Cl,HCl$ requires Cl, 34·0%). The following hydrazones were prepared and crystallised from glacial acetic acid; the colours developed in alcoholic potassium hydroxide are recorded after the analysis: *Benzaldehyde-3-chloroanisyl-2-hydrazone*, pale yellow prisms, m. p. 92° (Found: Cl, 13·4. $C_{14}H_{13}ON_2Cl$ requires Cl, 13·6%). o-*Nitrobenzaldehyde-3-chloroanisyl-2-hydrazone*, deep crimson rhombs, m. p. 131° (Found: Cl, 11·6. $C_{14}H_{12}O_3N_3Cl$ requires Cl, 11·6%); deep green in the cold, changed to emerald-green on heating. m-*Nitrobenzaldehyde-3-chloroanisyl-2-hydrazone*, yellow micro-crystals, m. p. 131° (Found: Cl, 11·4%); brown, changed to golden-brown on heating. p-*Nitrobenzaldehyde-3-chloroanisyl-2-hydrazone*, vermilion micro-prisms, m. p. 105° (Found: Cl, 11·4%); olive-green, changed to bright blue in the cold and to bluish-black on heating.

Dyes.—3-Chloro-2-aminoanisole was diazotised and coupled in the usual way with Schäffer, R- and N.W. acids in alkaline solution. With concentrated sulphuric acid the powdered dyes gave bright red, bluish-red, and violet colours respectively.

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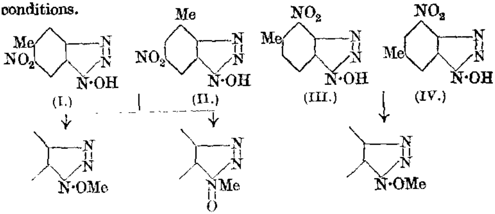
TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, November 24th*, 1927.]

XXIX.—*Triazole Compounds. Part II. Methylation of Some* 1-*Hydroxy*-1:2:3-*benztriazoles.*

By OSCAR L. BRADY and CEDRIC V. REYNOLDS.

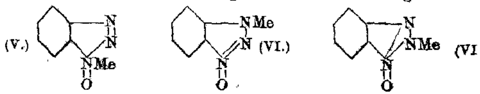
IN Part I (J., 1923, **123**, 2258) it was shown that 6-nitro-1-hydroxy-5-methyl- and 6-nitro-1-hydroxy-4-methyl-1:2:3-benztriazoles (I and II) on methylation gave mixtures of *O*- and *N*-methyl derivatives, the former greatly preponderating, whereas 4-nitro-1-hydroxy-5(or 7)-methyl- and 4-nitro-1-hydroxy-6-methyl-1:2:3-benztri-

azoles (III and IV) gave only *O*-methyl compounds under similar conditions.

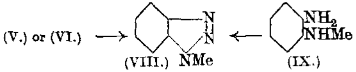


Since in (III) and (IV) the nitro-group in the ortho-position wit respect to the triazole ring may be expected to cause the compound to be stronger acids than (I) and (II), it seems likely that th mechanism of methylation is analogous to that for the oxim (Brady and Goldstein, J., 1926, 2403), that is, the formation of th *O*-methyl derivative is an ionic and of the *N*-methyl derivative molecular reaction. The former reaction would be favoured b employing a highly dissociated salt of a strong acid. Now th yield of the *N*-methyl compound in the above cases was small an if these views are correct, 1-hydroxy-1 : 2 : 3-benztriazole shou give a much larger proportion of the *N*-methyl derivative. This so, the ratio of *O*- to *N*-methyl derivative being about 1·6 to Moreover, when the methylation is carried out with the fr hydroxybenztriazole in non-ionising solvents the sole product the *N*-methyl compound, this reaction also being analogous to th of the aldoximes (Brady, Dunn, and Goldstein, J., 1926, 239 Further, 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole, which shou be a weaker acid than 1-hydroxy-1 : 2 : 3-benztriazole, gives a st larger proportion of *N*-methyl derivative, the ratio of *O*- to *N*-co pound being about 1·1 to 1. Methyl sulphate in aqueous alk produces a greater amount of *N*-compound, as compared w *O*-compound, than does methyl iodide in alcoholic sodium ethoxi but the same relative difference occurs between the two methods methylation as applied to 1-hydroxy-1 : 2 : 3-benztriazole a 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole.

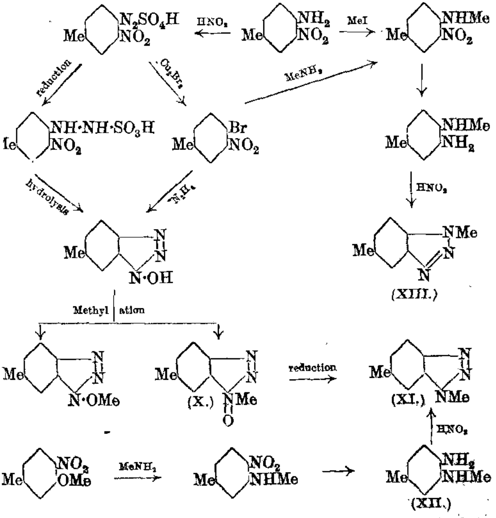
In Part I the constitution of the *N*-methyl compound was l undetermined, the choice being between the following formulæ



This problem has now been solved. Structure (VII) was rejected ecause the *N*-methyl compound on reduction gave 1-methyl- : 2 : 3-benztriazole (VIII), which is formed from methyl-phenylenediamine (IX) by the action of nitrous acid.



The choice fell finally on (V) as the result of the consideration of ıe reduction of 1 : 6-dimethyl-1 : 2 : 3-benztriazole 1-oxide (X) to : 6-dimethyl-1 : 2 : 3-benztriazole (XI), which was synthesised om 4-amino-3-methylaminotoluene (XII), the methyl group in ıe 6-position enabling a differentiation to be made between the · and the 3-position in the triazole ring. The reactions involved were ı follows :



3 : 6-Dimethyl-1 : 2 : 3-benztriazole (XIII) was synthesised in ıe unlikely event of (XI) and (XIII) being tautomeric and was ound to be quite distinct from (XI).

EXPERIMENTAL.

1-*Hydroxy*-1 : 2 : 3-*benztriazole*.—*o*-Nitrophenylhydrazine was first prepared by Bischler's method (*Ber.*, 1889, **22**, 2801), but a cleaner and more rapid way was one analogous to that used by Davies (*J.*, 1922, **121**, 715) for the preparation of the *p*-nitro-compound. A solution of *o*-nitroaniline (10 g.) in concentrated hydrochloric acid (21 c.c.) at 100° was cooled to 5° and diazotised (5 g. of sodium nitrite in 35 c.c. of water). The solution was then filtered from a small amount of brown precipitate and run, during 5 minutes, into a solution of crystallised sodium sulphite (41 g.) in *N*-sodium hydroxide (100 c.c.) cooled below 0°. The deep red solution after 5 minutes was treated with concentrated hydrochloric acid (70 c.c.) and warmed to 60°. After 3 minutes, yellow needles separated. The mixture was cooled and kept for 24 hours and the crystalline precipitate, which probably consisted of sodium *o*-nitrophenylhydrazinemonosulphonate, was then collected and heated with concentrated hydrochloric acid (20 c.c.) for 10 minntes on the water-bath. The hydrochloride of *o*-nitrophenylhydrazine that separated on cooling was dissolved in a small quantity of hot water, and a cold saturated solution of sodium acetate added. After cooling, the *o*-nitrophenylhydrazine (7 g.) was collected, washed with water, air-dried, and crystallised from alcohol. Replacing the sodium suphite by ammonium sulphite did not give such a good result, the mono-ammonium sulphonate being more soluble than the corresponding sodium salt.

1-Hydroxy-1 : 2 : 3-benztriazole was prepared in nearly theoretical yield by the action of 25% potassium hydroxide solution on o-nitrophenylhydrazine (Zincke and Schwarz, *Annalen*, 1900, **311**, 332), but it can conveniently be obtained from the intermediate product in the above preparation, sodium *o*-nitrophenylhydrazinemonosulphonate. This compound, after being freed from water as completely as possible by means of a water-pump, was boiled under reflux with alcohol (100 c.c.), and an alcoholic solution of potassium hydroxide (rather more than 2 mols.) run in during 30 minutes; the colour then changed from bright yellow through purple to light brown. The alcohol was removed by distillation, the residue dissolved in boiling water, the solution filtered, cooled, and acidified with concentrated hydrochloric acid, and the precipitated hydroxybenztriazole crystallised from hot water containing animal charcoal.

o-Bromonitrobenzene (5 g.) was boiled with alcohol (100 c.c.) and 50% hydrazine hydrate (15 c.c.) under reflux for 30 hours. After distillation of the alcohol, and of the unchanged bromonitrobenzene in steam, the aqueous residue was filtered, evaporated to a small bulk, and acidified with hydrochloric acid; the hydroxytriazole

was then precipitated in 60% yield. The addition of copper bronze during the boiling with hydrazine did not facilitate the reaction.

o-Bromonitrobenzene (5 g.) was heated with 50% hydrazine hydrate solution (10 c.c.) in a sealed tube at 160° for 6 hours. The solution, after being acidified with hydrochloric acid, neither gave a precipitate nor yielded anything to ether. From the solution, made alkaline, chloroform extracted 1 : 2 : 3-benztriazole. At the temperature used, the excess of hydrazine hydrate reduced the hydroxybenztriazole first formed.

1-Hydroxy-1 : 2 : 3-benztriazole is precipitated from a solution of its sodium salt at 0° as an unstable hydrate which loses water on drying in the air.

1-*Acetoxy*-1 : 2 : 3-*benztriazole* was obtained by warming the hydroxybenztriazole (1 g.) with acetic anhydride and one drop of concentrated sulphuric acid on the water-bath and pouring the cooled solution into a saturated solution of sodium carbonate at 0°; the solid obtained, after being washed once with water and dried immediately on a porous tile for a few minutes, crystallised from benzene, containing a few drops of acetic anhydride, in colourless prisms, m. p. 98° (Found : N, 23·7. $C_8H_7O_2N_3$ requires N, 23·7%). The compound is readily hydrolysed by warm dilute sulphuric acid; it decomposes in a few days when left exposed to the air and more slowly in a corked vessel. Nietzki and Braunschweig (*Ber.*, 1894, 27, 3381) and Zincke and Schwarz (*Annalen*, 1900, **311**, 332) were unable to obtain this acetyl compound and stated that acetic anhydride was without action on the hydroxybenztriazole.

1-*Benzoyloxy*-1 : 2 : 3-*benztriazole*, prepared from the hydroxybenztriazole (1 g.), 2*N*-sodium hydroxide (50 c.c.), and benzoyl chloride (5 g.), crystallised from benzene–light petroleum in colourless needles, m. p. 77° (Found : N, 17·8. $C_{13}H_9O_2N_3$ requires N, 17·6%). This compound, which was also prepared at 0° by the pyridine method of benzoylation, is more stable than the acetyl derivative, but decomposes slowly on exposure to air. On hydrolysis with dilute sulphuric acid, it gives benzoic acid and hydroxybenztriazole.

Reduction of the hydroxybenztriazole. Zincke and Schwarz (*loc. cit.*), by heating the hydroxybenztriazole with hydriodic acid in a sealed tube at 140—150°, obtained a polyiodide of 1 : 2 : 3-benztriazole; but if it (2 g.) is heated with hydriodic acid (6 c.c.; *d* 1·7) and red phosphorus (4 g.) in a sealed tube at 140—150° for 4 hours no polyiodide is formed. After dilution, filtration, evaporation to half bulk, neutralisation with a saturated solution of sodium carbonate, and extraction with chloroform, an almost quantitative yield of 1 : 2 : 3-benztriazole was obtained, which was identified by

conversion into its acetyl derivative and comparison with a specimen prepared from *o*-nitroacetanilide by Bell and Kenyon's method (*J.*, 1926, 954).

Methylation of 1-*Hydroxy*-1 : 2 : 3-*benztriazole*.—There is no mention in the literature of the methylation of the hydroxybenztriazole, but Nietzki and Braunschweig (*Ber.*, 1894, **27**, 3382) stated that ethyl iodide had no action, even at a high temperature.

With methyl sulphate. When the hydroxybenztriazole (2 g.) in 2*N*-sodium hydroxide (50 c.c.) was treated with methyl sulphate (6 g.) in small portions with constant shaking, the temperature rose to 60° and a small amount of white solid separated. The mixture was warmed on the water-bath to complete the reaction and then distilled in steam. The aqueous distillate, in which crystals were floating, was extracted with chloroform and after drying and removal of the solvent the residual oil solidified on cooling. After crystallising from alcohol, 1-*methoxy*-1 : 2 : 3-*benztriazole* was obtained in colourless needles, m. p. 89° (Found: N, 28·2; OMe, 20·2. $C_7H_7ON_3$ requires N, 28·2; OMe, 20·8%). The average yield from a number of experiments was 0·8 g.

From the aqueous residue in the distilling flask, after concentration, repeated extraction with chloroform removed 1-*methyl*-1 : 2 : 3-*benztriazole* 1-*oxide*, which crystallised from alcohol or benzene–light petroleum in colourless needles, m. p. 145° (Found: N, 28·1. $C_7H_7ON_3$ requires N, 28·2%). The average yield was 0·4 g. On heating this compound with hydriodic acid, no methyl iodide was evolved.

The aqueous residue after the chloroform extraction was acidified and the precipitate of unchanged hydroxybenztriazole was collected, dried, and weighed, the average amount being about 0·5 g.; 25% of the triazole is unaccounted for and this loss is probably due to the solubility of the hydroxybenztriazole and the methylbenztriazole 1-oxide in water and to the difficulty of extracting the latter therefrom by chloroform.

The hydroxybenztriazole (1 g.) was heated with pure methyl sulphate (10 g.) at 100° for several hours; after cooling, the addition of ether precipitated an oil, presumably a methosulphate. As this would not crystallise, it was hydrolysed by boiling with dilute hydrochloric acid; the solution then contained sulphuric acid and on exhaustive extraction with chloroform yielded almost pure 1-methyl-1 : 2 : 3-benztriazole 1-oxide. A similar result was obtained when the hydroxybenztriazole was sealed up with methyl sulphate and kept in the dark for 10 weeks (compare Brady, Dunn, and Goldstein, *loc. cit.*).

With methyl iodide. A solution of the hydroxybenztriazole (3 g.),

sodium ethoxide (prepared from 0·35 g. of sodium), and methyl iodide (8 g.) in absolute alcohol was boiled under reflux for 2 to 3 hours. The alcohol was then removed by distillation, and the residue distilled in steam. The aqueous distillate on extraction with chloroform yielded 1·5 g. of the *O*-methyl ether, and the solution remaining in the flask, after being evaporated to small bulk and extracted with chloroform, gave 0·5 g. of 1-methyl-1 : 2 : 3-benztriazole 1-oxide. The aqueous layer, on being acidified, gave no hydroxybenztriazole, indicating complete methylation.

Methylation of the silver salt of the hydroxybenztriazole in alcohol gave a large amount of O-ether and only a small quantity of the *N*-methyl compound, and a similar result was obtained by methylation in dry benzene with methyl iodide and dry silver oxide.

The hydroxybenztriazole (1 g.), sealed up with methyl iodide (10 g.), was kept in the dark for 2 months. Some iodine was liberated and the liquid contained dark crystals. Excess of ether was added and the precipitated dark oil was treated with dilute sodium hydroxide solution and a little sodium thiosulphate to destroy free iodine. On distilling in steam no *O*-ether was obtained, so the solution was evaporated to small bulk and extracted with chloroform; the *N*-methyl compound was then obtained. The ethereal solution was evaporated and the residue was treated with dilute sodium hydroxide solution and sodium thiosulphate and distilled in steam, but no *O*-ether was found in the distillate.

Synthesis of 1-*Methyl*-1 : 2 : 3-*benztriazole*.—*o*-Nitromethylaniline has been prepared by previous workers in a number of ways, usually involving sealed tubes. Nitration of methylaniline with copper nitrate trihydrate in acetic anhydride (Menke, *Rec. trav. chim.*, 1925, **44**, 141, 269) was not successful, but the following method, analogous to that of Witt and Utermann (*Ber.*, 1906, **39**, 3903), gave satisfactory results. A mixture of acetic anhydride (3 c.c.), nitric acid (5 c.c.; *d* 1·5), and a small quantity of urea at 0° was slowly added, with mechanical stirring, to methylacetanilide (10 g.) suspended in acetic anhydride (10 c.c.), the temperature being kept below 10°. After being kept at room temperature for 24 hours, the solution was poured into cold water and just neutralised with concentrated ammonium hydroxide. The oil thus produced was extracted with chloroform and boiled under reflux for 2 hours with 50% sulphuric acid (100 c.c.), the red solution being then distilled in steam. The aqueous distillate (2·5—3 l.) on extraction with chloroform gave 5 g. of *o*-nitromethylaniline.

1-*Methyl*-1 : 2 : 3-*benztriazole*. The isolation of the unstable methyl-*o*-phenylenediamine was unnecessary. The following method of reducing *o*-nitromethylaniline is a great improvement on

that of Fischer using tin and hydrochloric acid (*Ber.*, 1892, **25**, 2841). *o*-Nitromethylaniline (5 g.) was suspended in boiling water (75 c.c.), and a solution of sodium hydrosulphite run in slowly until the colour vanished. The solution was made alkaline with sodium hydroxide and extracted with benzene, and the extract shaken with an equal volume of 20% hydrochloric acid. The acid solution of methyl-*o*-phenylenediamine hydrochloride so obtained was cooled to 0° and sodium nitrite (1 g. in 7 c.c. of water) added and when the action was complete the mixture was boiled for 30 minutes. No dark-coloured by-product was obtained as mentioned by Reissert (*Ber.*, 1914, **47**, 676). After cooling, the acid solution was neutralised with sodium carbonate and extracted with chloroform. Removal of the solvent gave an almost theoretical yield of crude 1-methyl-1 : 2 : 3-benztriazole, which was crystallised from benzene–light petroleum.

1-Methyl-1 : 2 : 3-benztriazole 1-oxide (1 g.) was boiled with hydriodic acid (15 c.c.; *d* 1·7) and red phosphorus (3 g.) for 6 hours. The solution was diluted, filtered, made alkaline with sodium hydroxide, and decolorised with sodium thiosulphate. On extraction with chloroform and crystallisation from benzene–light petroleum, 1-methyl-1 : 2 : 3-benztriazole was obtained identical with the above compound.

1-*Hydroxy*-6-*methyl*-1 : 2 : 3-*benztriazole*.—This compound was prepared in an analogous manner to hydroxybenztriazole, but ammonium sulphite gives in this case a better result than sodium sulphite (compare Zincke and Schwarz, and Davies, *locc. cit.*). 4-Bromo-3-nitrotoluene (5 g.), prepared by the Sandmeyer method from 3-nitro-*p*-toluidine (compare Nevile and Winther, *Ber.*, 1880, **13**, 972), was boiled under reflux with alcohol (100 c.c.) and 50% hydrazine hydrate (20 c.c.) for 30 hours, the alcohol distilled off, and the residue distilled in steam. The solution remaining in the flask was filtered while hot, acidified with concentrated hydrochloric acid, and evaporated to small bulk; on cooling, 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole crystallised in 60% yield. One crystallisation from water gave the pure compound.

Acetyl and benzoyl derivatives of 1-*hydroxy*-6-*methyl*-1 : 2 : 3-*benztriazole*. These compounds were obtained in good yield in similar ways to the corresponding hydroxybenztriazole compounds and have similar properties. 1-*Acetoxy*-6-*methyl*-1 : 2 : 3-*benztriazole* crystallised from benzene, containing a little acetic anhydride, in colourless prisms, m. p. 138° (Found: N, 22·4. $C_9H_9O_2N_3$ requires N, 22·0%). 1-*Benzoyloxy*-6-*methyl*-1 : 2 : 3-*benztriazole* crystallised from benzene–light petroleum in colourless prisms, m. p. 129—130° (Found: N, 17·0. $C_{14}H_{11}O_2N_3$ requires N, 16·6%).

Reduction of 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole. This was carried out as in the case of the hydroxybenztriazole and a good yield of 6-methyl-1 : 2 : 3-benztriazole, identified by comparison with a specimen prepared from 3 : 4-tolylenediamine (Ladenburg, *Ber.*, 1876, **9**, 220), was obtained.

Methylation of 1-Hydroxy-6-methyl-1 : 2 : 3-benztriazole.—*With methyl sulphate.* On methylation with methyl sulphate in the presence of 2*N*-sodium hydroxide in exactly the same way as hydroxybenztriazole, 2 g. of 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole gave 0·52 g. of *1-methoxy-6-methyl-1 : 2 : 3-benztriazole*, which crystallised from alcohol in colourless needles, m. p. 50° (Found : N, 26·1; OMe, 18·3. $C_8H_9ON_3$ requires N, 25·8; OMe, 19·0%). At the same time, there was obtained 0·47 g. of *1 : 6-dimethyl-1 : 2 : 3-benztriazole 1-oxide*, which crystallised from benzene–light petroleum in colourless needles, m. p. 169° (Found : N, 26·0. $C_8H_9ON_3$ requires N, 25·8%). The unmethylated triazole recovered was 0·41 g. As the result of a number of experiments it was found that the ratio of *O*-ether to *N*-methyl-*N*-oxide was less than that for the unsubstituted hydroxybenztriazole. Heating 1-hydroxy-6-methyl-1 : 2 : 3-benztriazole with pure methyl sulphate or keeping it with that reagent for 10 weeks also yielded the *N*-methyl-*N*-oxide and no *O*-ether.

With methyl iodide. By the same method, similar results were obtained to those with hydroxybenztriazole : 2 g. gave 0·84 g. of *O*-methyl ether and 0·4 g. of *N*-methyl-*N*-oxide. Results similar to those with the unsubstituted compound were obtained by using the silver salt, methyl iodide alone or methyl iodide in benzene with silver oxide.

1 : 6-Dimethyl-1 : 2 : 3-benztriazole.—Zincke and Lawson (*Annalen*, 1887, **240**, 126) claim to have prepared a dimethyl-1 : 2 : 3-benztriazole, but their compound, of which they give no analysis, was probably a mixture of 1 : 6- and 3 : 6-dimethyl-1 : 2 : 3-benztriazole. The following method for preparing the initial material, 4-nitro-*m*-tolyl methyl ether, is a great improvement on those previously described (Reissert, *Ber.*, 1898, **31**, 397; Khotinsky and Jacopson-Jacopmann, *Ber.*, 1909, **42**, 3100). A mixture of 4-nitro-*m*-cresol, methyl iodide (15 g.), dry benzene (75 c.c.), and dry, freshly prepared silver oxide (10 g.) was boiled under reflux for 3 hours. The benzene was distilled off, water and 5 c.c. of 2*N*-sodium hydroxide were added, and the product was distilled in steam. 4-Nitro-*m*-tolyl methyl ether crystallised from the distillate in almost theoretical yield. It is best recrystallised from light petroleum. 4-Nitro-3-methylaminotoluene (3 g.), prepared from the above by heating to 165° with methylamine (Fischer and Rigaud, *Ber.*,

1902, **35**, 1260), was suspended in boiling water (50 c.c.) and reduced with sodium hydrosulphite as in the preparation of 1-methyl-1 : 2 : 3-benztriazole. The hydrochloric acid solution of 4-amino-3-methylaminotoluene was diazotised by the addition below 5° of sodium nitrite (1 g. in 7 c.c. of water). (It is important to keep the solution for 30 minutes to complete the reaction.) After treatment as before, 1 : 6-*dimethyl*-1 : 2 : 3-*benztriazole* was obtained from benzene–light petroleum in colourless plates, m. p. 75° (Found: N, 28·7. $C_8H_9N_3$ requires N, 28·6%). When 1 : 6-dimethyl-1 : 2 : 3-benztriazole 1-oxide was reduced with hydriodic acid in an exactly similar manner to 1-methyl-1 : 2 : 3-benztriazole 1-oxide, a compound identical with the above 1 : 6-dimethyl-1 : 2 : 3-benztriazole was obtained.

3 : 6-*Dimethyl*-1 : 2 : 3-*benztriazole*.—This compound was prepared for comparison by the reduction of 3-nitro-4-methylaminotoluene with sodium hydrosulphite, followed by the action of nitrous acid as before. The initial material is best prepared by heating 4-bromo-3-nitrotoluene (see above) (10 g.) with 33% aqueous methylamine (15 c.c.) for 6 hours in a sealed tube at 150°. The solid product left in the tube, on crystallisation from alcohol, gave 7 g. of pure 3-nitro-4-methylaminotoluene. Gattermann's method (*Ber.*, 1885, **18**, 1487) gave poor yields. 3 : 6-*Dimethyl*-1 : 2 : 3-*benztriazole* crystallised from benzene–light petroleum in colourless plates, m. p. 50° (Found: N, 28·9. $C_8H_9N_3$ requires N, 28·6%).

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XXX.—*The Structure of the Platinicyanides: The Potential of the Platino–Platinicyanide Electrode.*

By HENRY TERREY.

WHEN a concentrated solution of potassium platinocyanide, $K_2Pt(CN)_4$, is anodically oxidised with a platinum electrode (preferably platinised) and a low *C.D.*, a characteristic, dark brown product separates at the anode (Wilm, *Ber.*, 1888, **21**, 1434). This compound, which has the empirical formula $K_7Pt_4(CN)_{16},6H_2O$, is generally regarded as a platinoplatinicyanide

$$3K_2Pt(CN)_4,KPt(CN)_4,6H_2O;$$

the platinicyanides would thus differ from the platini-halogen salts in containing tervalent platinum. The same compound has also been obtained by Levy (J., 1912, **101**, 1081) by the action of

hydrogen peroxide (20 vol.) on a potassium platinicyanide solution. By repeated treatment of a concentrated platinocyanide solution with acidified perhydrol, Levy obtained the completely oxidised compound $KPt(CN)_4$; the conditions necessary for its preparation seem to be very critical, and it was not found possible to repeat it. Moreover, a more completely oxidised compound than Wilm's salt could not be prepared electrolytically, although both high and low *C.D.*'s at different temperatures were used. From a concentrated solution the dark brown product always separated. When more dilute solutions were used, so that no solid appeared at the anode, oxidation never proceeded to a greater extent than approximately one-sixth of the platinocyanide present. In order to obtain further information on the nature of the platinicyanides, it was decided to investigate the platino–platini electrode, and in the determination of the potentials of this electrode Wilm's salt together with pure potassium platinocyanide, was used.

When a noble-metal electrode is inserted in a solution of Wilm' salt and platinocyanide, a definite and reproducible *P.D.* is slowl set up, attaining a maximum at the end of 1—2 hours and ther remaining steady for many hours. The current produced tends t flow through the electrolyte from the calomel to the platino–platin electrode.

On the assumption that the platino–platini salts are of the sam type as the ferro–ferri salts (Wilm, Levy), the reaction taking plac at the electrode can be represented by $Pt^{III}(\bar{CN})_4 + \ominus \longrightarrow Pt^{II}(\bar{\bar{CN}})_4$ The equation for the electrode *P.D.* is thus $E = E_0 + RT/F \,.\, \log a_i/a_o$ where a_i and a_o are the activities of the platini- and platino ions, respectively. In the presence of excess and constant amoun of electrolyte (*N*-potassium chloride), one can assume that the rati of the activities of the platinum salts is equal to the ratio of thei concentrations (i and o, respectively), *i.e.*, $a_i/a_o = i/o$, and th equation takes the form $E = E_0 + RT/F \,.\, \log i/o$.

Experimental.

The electrode solutions were prepared by weighing out th requisite amounts of the two salts and dissolving in *N*-potassiun chloride. An ordinary type half cell was used in conjunction with normal calomel electrode. Platinised glass or platinum points wer used as electrodes, although with the latter, owing to the smal capacity, polarisation effects were very marked, and the determin ation of the null point was troublesome. The measuring apparatu consisted of a Weston standard cell, a Kohlrausch rotating bridge and a Cambridge moving-coil galvanometer.

Results.

In Table I is shown the effect of concentration on the *E.M.F.* at 15°, the ratio platino : platini being kept constant at 3 : 1 by the use of Wilm's salt alone. It will be noticed that there is a small fall in the *E.M.F.* with decreasing total concentration.

TABLE I.

Conc. of Wilm's salt (mg./l.) ...	293·0	195·3	130·2	82·1	47·0
E.M.F. of cell	0·5898	0·5894	0·5883	0·5879	0·5852

In Table II are given the potentials of the electrode when the ratio platino : platini is changed from 3 : 1 to 53 : 1, the concentration of the latter being kept constant. In column 3 are the values of E_0 when calculated according to the last equation (above).

TABLE II.

Ratio, mols. platino : platini.	*E.M.F. of electrode* (Calomel = 0·2870 volt).	E_0, volt.	E_0', volt.
3·00	0·8748	0·9016	0·8884
4·47	0·8690	0·9054	0·8872
9·45	0·8594	0·9140	0·8867
9·86	0·8580	0·9137	0·8858
13·68	0·8542	0·9178	0·8860
52·65	0·8410	0·9374	0·8893

It will be noticed that E_0 progressively increases instead of giving the expected constant. If, however, the equation $E = E_0' + RT/2F \, . \log i/o$ is used, which differs only in the value of n, the values under E_0' are obtained. These are much more constant and suggest that in the conversion of the platinocyanide into the platinicyanide there is a valency change from 2 to 4 instead of from 2 to 3, although this form of equation cannot represent the electrochemical changes in these circumstances.

There is little doubt that the empirical formula of Wilm's salt is best represented by $K_7Pt_4(CN)_{16},6H_2O$, as is evident from the author's analyses and those of Wilm and Levy :

	K.	Pt.	CN.	H_2O.	Iodine liberated per g. of salt.
Theory	17·34	49·46	26·4	6·86	0·0804 g.
Wilm	17·2	49·4	—	6·96	—
Levy	17·1	49·2	24·9	6·9	0·0800
Author	17·1	49·6	27·0	7·1	0·0821

If electrolytic oxidation of potassium platinocyanide is carried out in the presence of hydrochloric acid, a chloro-compound similar in properties to Wilm's salt is obtained. This has the composition $[3K_2Pt(CN)_4]Cl,9H_2O$ (Hadow, J., 1861, **13**, 106; Wilm, *loc. cit.*). If oxidation with metallic peroxides is carried out in the presence of sulphuric acid, a sulphate is obtained with the composition

$[xK_2Pt(CN)_4]SO_4$, x being probably 9. The latter behaves as the sulphate of a feebly electronegative metal, undergoing decomposition with barium salts. With barium platinocyanide it gives a platinocyanide of the type $[xK_2Pt(CN)_4]Pt(CN)_4$ (Levy, *loc. cit.*).

The halogen compounds can also be prepared by mixing potassium platinocyanide with the corresponding per-halogen salt $K_2Pt(CN)_4X_2$. This indicates that these complexes are best represented by the formula $[xK_2Pt(CN)_4]KPt(CN)_4X_2$; Wilm's measurements of the molecular weight in acetic acid show that in solution they are dissociated into the simple salts (*Ber.*, 1889, **22**, 1546).

In view of the potential measurements, the so-called completely oxidised platinocyanide product is better represented by the formula $K_2Pt^{IV}(CN)_4,Pt^{II}(CN)_4$ than by the simple formula

$$KPt^{III}(CN)_4.$$

This compound is thus analogous to the perchloro-salt $K_2Pt^{IV}(CN)_4Cl_2$, the radical $Pt^{II}(CN)_4$ having replaced 2 atoms of chlorine, and is a derivative of the true platinicyanides $K_2Pt^{IV}(CN)_6$ in which a molecule of cyanogen has been replaced by $Pt^{II}(CN)_4$.

Further evidence in support of this view of the structure of the platinicyanides is given by the behaviour of Wilm's salt towards acids and alkalis and halogens.

In solution, Wilm's salt adds on 2 mols. of halogen acid or alkali chloride. Considering only the oxidised part of Wilm's salt, this addition is most easily explained as follows: In solution the salt is hydrolysed with the production of a hydroxy-compound:

$$K_2Pt^{IV}(CN)_4,Pt^{II}(CN)_4+H_2O \longrightarrow H_2Pt^{IV}(CN)_4(OH)_2+K_2Pt^{II}(CN)_4;$$

this hydroxy-compound may be compared with the corresponding chloro-derivative $H_2Pt^{IV}(Cl_4)(OH)_2$. The cyano-hydroxy-compound behaves in the same way towards halogen acids and alkali halides, forming the chloro-cyano-compound, *e.g.*, $H_2Pt^{IV}(CN)_4(OH)_2 + 2HCl = H_2Pt^{IV}(CN)_4Cl_2 + 2H_2O$. Halogens convert Wilm's salt into the corresponding per-halogen derivative. Levy explains this action on the supposition that the halogen reduces the platinicyanide to the platino-salt, which is then halogenated:

$$KPt(CN)_4 \longrightarrow KHPt(CN)_4 \longrightarrow KHPt(CN)_4X_2.$$

It is difficult to see why halogens should act here as reducing agents. The halogenation of the hydroxy-compound is, however, simple to follow. If Wilm's salt is regarded as

$$6K_2Pt^{II}(CN)_4,K_2Pt^{IV}(CN)_4Pt^{II}(CN)_4,$$

it is seen that the ratio platino : platini is 7 : 1. In the potential measurements the reaction of the cell is given by the equation $K_2Pt^{IV}(CN)_4Cl_2 + 2Hg \rightleftharpoons 2HgCl + K_2Pt^{II}(CN)_4$ [since dissolution

of *Wilm's salt in potassium chloride* gives rise to $K_2Pt(CN)_4Cl_2]$. The electrode reaction is $[Pt(CN)_4Cl_2]^{--} + 2e = [Pt(CN)_4]^{--} + 2\bar{Cl}$, and the *E.M.F.* is given by $E = E_0 + RT/2F . \log a_y/a_z a^2_{Cl}$, where a_y = activity of chlorocyanide $[Pt(CN)_4Cl_2]$ ion; a_z = activity of platinocyanide $[Pt(CN)_4]$ ion; a_{Cl} = activity of the chlorine ion. In the presence of excess and constant amount of electrolyte, this leads to the expression $E = E_0 + RT/2F . \log c_y/c_z a^2_{Cl}$, where c_y and c_z are the concentrations of the platinichlorocyanide and platinocyanide, respectively.

Table III shows the value of E_0 calculated according to the above expression from measurements at 13°, the value of a_{Cl} in *N*-potassium chloride being taken as 0·634. The values are reasonably constant, and the slight fall may be due to incomplete splitting of Wilm's salt in the presence of a large excess of platinocyanide.

TABLE III.

Ratio, platini : platino.	*Reduction potential of electrode.*	E_0.
1 : 7	0·8749	0·8881
1 : 9·95	0·8690	0·8865
1 : 19·90	0·8594	0·8860
1 : 21·51	0·8580	0·8856
1 : 28·40	0·8542	0·8854
1 : 69·40	0·8410	0·8840

Summary.

From measurements of the potential of the platini–platino electrode, it is shown that in the so-called platinicyanides part of the platinum is present in the quadrivalent state and not in the tervalent state.

These salts are more correctly represented by the formula $K_2Pt^{IV}(CN)_4Pt^{II}(CN)_4$ than by $KPt^{III}(CN)_4$.

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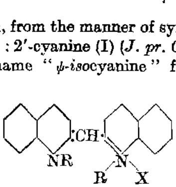
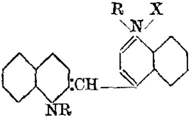
XXXI.—*The ψ-Cyanine Condensation.*

By FRANCES MARY HAMER.

IT has been recorded by Kaufmann that a red dye is very slowly formed by the action of potassium hydroxide on an alcoholic solution of 2-iodoquinoline ethiodide and quinaldine ethiodide (*Ber.*, 1912, **45**, 1417). By a modification of his method, Fischer and Scheibe succeeded in isolating the corresponding methiodide, to

which, from the manner of synthesis, they assigned the constitution of a 2 : 2′-cyanine (I) (*J. pr. Chem.*, 1919, **100**, 86). They proposed the name "ψ-*iso*cyanine" for dyes of this type, but the term

(I.) 

 (II.)

"ψ-cyanine," as used by Mills and Odams (J., 1924, **125**, 1913), is preferable. Fischer and Scheibe attributed the low yield of ψ-cyanine obtained by Kaufmann to decomposition of the 2-iodoquinoline alkyliodide by alcohol; they state that this decomposition is diminished by a suitable selection of the solvent, and that by dissolving the alkyliodides in dilute hydrochloric acid and adding potassium hydroxide, a 40% yield of pure ψ-cyanine is obtainable. Exact details are not, however, given, and attempts to reproduce this yield proved unsuccessful.

It is indeed true, as previously noted by Roser (*Annalen*, 1894, 282, 373), that 2-iodoquinoline methiodide is unstable. But it is now found that acid, far from the power attributed to it, has the effect of increasing this instability, so that its use as solvent is clearly undesirable. In the earlier of the present preparations, the method consisted in adding a slight excess of potassium hydroxide to a boiling aqueous solution of the alkyliodides, and the maximum yield of pure product so obtained was about 20% of that theoretically possible. By using absolute alcohol as solvent, the yields are approximately doubled. If rectified spirit is used, there is a tendency to the formation of impurities of the carbocyanine type.

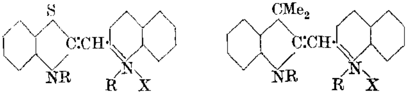
Hitherto only two ψ-cyanines have been prepared (Fischer, *J. pr. Chem.*, 1918, **98**, 204; Fischer and Scheibe, *loc. cit.*), and it is curious, in view of the importance of other cyanine dyes as photographic sensitisers, that no examination of their photographic properties has been recorded. Eight ψ-cyanines are now described, of which seven are new, and Mr. O. F. Bloch has examined their absorption spectra in alcoholic solution and has studied their photographic action, both by bathing plates in solutions of the dyes and also by adding the latter to the emulsion before coating. He has found that the ψ-cyanines exert a sensitising action in the bluish-green region of the spectrum, and that certain of them are of practical value.

The ψ-cyanine reaction may be applied to the preparation of other cyanine dyes. Thus by condensation of lepidine alkyliodide with

2-iodoquinoline alkyliodide, an *iso*cyanine is produced, and this new method of synthesis confirms the now well-established formula (II) for *iso*cyanine.

To one of the reaction products which Mills and Braunholtz obtained by heating quinaldine ethonitrate with di-*o*-formylethylaminodiphenyl disulphide in pyridine solution they assigned formula (III) (J., 1923, **123**, 2804). This structure is now confirmed by the synthesis of this and three new thio-ψ-cyanines by condensation of 1-methylbenzthiazole alkyliodide with 2-iodoquinoline alkyliodide.

(III.) (IV.)



The method has been further extended to the synthesis of two dyes of a new type, for which the name indo-ψ-cyanine is proposed: for this preparation, 2-iodoquinoline alkyliodide is condensed with a substituted indolenine quaternary salt containing a reactive 2-methyl group. The formula (IV) is written as though the acid radical were attached to what is presumably the more basic part of the molecule (compare Mills and Wishart, J., 1920, **117**, 579).

The nomenclature of the ψ-cyanines requires consideration. Mills and Pope originated the system of affixing dashes to the numerals in the quinoline, as opposed to the quinaldine, nucleus of *iso*cyanine (*Phot. J.*, 1920, **44**, 183). According to the structure of *iso*cyanine (II) as established by Mills and Wishart (*loc. cit.*), this results in attaching dashes to the numerals in the nucleus which bears the acid radical, so that in the case of the thio-ψ-cyanines and indo-ψ-cyanines the dashes should follow the numerals in the quinoline nucleus; this system has apparently been adopted by Mills and Braunholtz (*loc. cit.*), although it is not specifically stated. With the ψ-cyanines themselves, however, the two nuclei are identical, and it is not possible to differentiate between them, so that alternative formulæ must be given. It is moreover found that the ψ-cyanine prepared from quinaldine methiodide and 2-iodoquinoline ethiodide has the same optical and photographic properties, etc., as that prepared from quinaldine ethiodide and 2-iodoquinoline methiodide; similarly, with the ψ-cyanines prepared from *p*-toluquinaldine methiodide and 2-iodoquinoline methiodide and from quinaldine methiodide and 2-iodo-6-methylquinoline methiodide the photographic properties are identical. Thus virtual tautomerism apparently occurs here, as in the case of the thiocyanines (Mills and Braunholtz, J., 1922, **121**, 1489).

EXPERIMENTAL.

2-*Iodoquinoline Methiodide*.—Roser prepared the iodide by heating 2-chloroquinoline and methyl iodide in a sealed tube (*loc. cit.*); but since methyl chloride is evolved, a considerable pressure develops, so that even with small-scale preparations loss through bursting of the tube is liable to occur: moreover, the product is contaminated by periodide. A higher yield of almost pure product is obtainable by prolonged heating in an open vessel: chloroquinoline (10 g.) and methyl iodide (15 c.c.) were heated in a water-bath, in a flask fitted with a reflux condenser and protected from the light, for 10 days. The product was extracted with ether in order to remove unchanged base and was thus obtained in 92% yield (Found: I, 63·3%) and, for the condensations, this salt was used without further purification. A specimen was rapidly recrystallised from water, dried in the steam-oven, and analysed by the method of Carius (Found: I, 64·1. Calc. for $C_{10}H_9NI_2$: I, 63·9%). It melted at 211—212°, as recorded by Roser. To test the influence of dilute acid on its stability, the crude iodide (1 g.) was added to boiling water (50 c.c.) and the solution was boiled for 5 minutes, filtered, and cooled; the iodide then crystallised (0·61 g.). A similar experiment was carried out, 5% hydrogen chloride solution (50 c.c.) being used, but this on cooling deposited only a black product (0·05 g.). It is therefore clear that dilute acid decreases the stability of 2-iodoquinoline methiodide.

2-*Iodoquinoline Ethiodide*.—On heating 2-chloroquinoline with ethyl iodide in a sealed tube by Roser's method, the yields are 35% and 49%, respectively, of that theoretically possible, according as heating is continued for 2 or for 4 days. But when a solution of the base (10 g.) in ethyl iodide (15 c.c.) is boiled under reflux for 10 days, the yield is 81%. After recrystallisation from water, the salt has m. p. 205° (decomp.), whereas Roser gives m. p. 220° (Found: I, 61·9. Calc. for $C_{11}H_{11}NI_2$: I, 61·8%).

1 : 6-*Dimethyl-2-quinolone*.—This was prepared by oxidising a solution of 6-methylquinoline methiodide by means of alkaline potassium ferricyanide at 0—7°. After extraction with chloroform and recrystallisation from benzene, a 70% yield resulted, but the compound melted at 82—84° with previous softening, whereas Fischer records the m. p. as 90° (*Ber.*, 1899, **32**, 1297). The quinolone was therefore distilled in a vacuum, by which, however, the m. p. was unaltered; b. p. 205°/15 mm. (Found: C, 76·3; H, 6·5; N, 8·0. Calc. for $C_{11}H_{11}ON$: C, 76·3; H, 6·4; N, 8·1%).

2-*Chloro-6-methylquinoline*.—This was prepared from 1 : 6-dimethyl-2-quinolone by a method analogous to that used by Perkin and Robinson for preparing 2-chloroquinoline (J., 1913, **103**, 1973).

The base cannot be purified by steam distillation, as recommended by Fischer (*loc. cit.*), first because it is only slightly volatile with steam and, further, because it solidifies in the condenser and remains unmelted at 100°. It was therefore extracted with benzene and after removal of the solvent the residue was recrystallised from spirit and then from petrol. As the melting point was still below that recorded by Fischer, the base was purified by crystallisation of its picrate, but even after this it melted at 111—112°, whereas Fischer gives m. p. 116°. It was dried in a vacuum desiccator before analysis (Found: Cl, 20·1. Calc. for $C_{10}H_8NCl$: Cl, 20·0%).

2-Iodo-6-methylquinoline methiodide was best obtained by heating 2-chloro-6-methylquinoline (3 g.) and methyl iodide (3 c.c.) for 2 days in a sealed tube at 100°. After ether extraction, the residue (87% yield) was recrystallised from water; the yield was then 52% and m. p. about 225° (decomp.) (Found: I, 61·75. $C_{11}H_{11}NI_2$ requires I, 61·8%).

1 : 1′-*Dimethyl-ψ-cyanine Iodide.*—This dye has been prepared by Fischer and Scheibe (*loc. cit.*). By the present method, crude 2-iodoquinoline methiodide (4 g.; 1 mol.) was added to boiling water (200 c.c.), and the solution filtered from periodide. Quinaldine methiodide (2·9 g.; 1 mol.) was added to the filtrate and the boiling solution was treated with an aqueous solution (30 c.c.) of potassium hydroxide (1·2 g.; more than 2 mols.). The dye separated (30% yield) and was recrystallised from rectified spirit; the yield was 21% of the theoretical. In another preparation, 2-iodoquinoline methiodide (12 g.) and quinaldine methiodide (8·6 g.) were boiled with absolute alcohol (600 c.c.) and an absolute alcoholic solution (60 c.c.) of potassium hydroxide (4·0 g.) was added; after ½ hour's boiling, all undissolved solid had disappeared. The product (52% yield) was obtained in 39% yield on recrystallisation. From spirit, the *iodide* separates as compact pleochroic green and purple crystals, and from methyl alcohol as small, red crystals. Its m. p. (not previously recorded) is at 245—246° (decomp.). It was dried under reduced pressure at 100—120° and analysed by the method of Carius, which method of drying and analysis were used throughout this work, except where otherwise stated (Found: I, 29·6. Calc. for $C_{21}H_{19}N_2I$: I, 29·8%). On bathing a plate in its solution, fairly strong extra sensitivity, extending to λ 6000 Å., is produced, with a maximum at λ 5600, but in the emulsion the sensitising action is less powerful.

1 (or 1′)-*Methyl*-1′ (or 1)-*ethyl-ψ-cyanine Iodide.*—This was prepared by the action of potassium hydroxide on an aqueous solution of 2-iodoquinoline methiodide and quinaldine ethiodide and, after recrystallisation from rectified spirit, was obtained in

13% yield, but by carrying out the preparation in alcoholic solution the yield was 33% (Found: I, 28·7. $C_{22}H_{21}N_2I$ requires I, 28·8%). Alternatively, 2-iodoquinoline ethiodide and quinaldine methiodide were condensed in absolute-alcoholic solution: the yield of recrystallised product was 28% (Found: I, 28·8%). By each method, the product was in the form of small, bronze crystals with a green lustre and both specimens and their mixture, when heated simultaneously, melted at 261—262° (decomp.). Their actions on photographic plates on bathing are identical. The first specimen, when added to an emulsion, behaves as a powerful sensitiser, giving a crest at λ 5800 which falls sharply to zero at λ 6000; there is a slight gap between the ordinary and the extra sensitivity, with its minimum at λ 5300. With bathed plates, the maximum is at λ 5750 and the gap is less, so that the rise to the crest is more gradual and the crest appears less marked.

1 : 1′ : 6 (or 1 : 1′ : 6′)-*Trimethyl-ψ-cyanine Iodide*.—By the first method, the interactants were 2-iodoquinoline methiodide and *p*-toluquinaldine methiodide, which were condensed in aqueous solution. On recrystallising the crude product (21% yield) from rectified spirit, fine, purple crystals were obtained, m. p. at about 220° (decomp.) (Found: I, 28·9. $C_{22}H_{21}N_2I$ requires I, 28·8%). On bathing, the dye confers on a plate a fairly uniform sensitisation, with a slight depression at λ 5300 and a maximum at λ 5500, decreasing gradually to zero at λ 6200, but when the compound is used in the emulsion, the extra sensitivity is less. By the second method of preparation, 2-iodo-6-methylquinoline methiodide and quinaldine methiodide were condensed in absolute alcoholic solution, and a 33% yield of recrystallised product resulted (Found: I, 28·8%). The crystals were redder than those obtained previously and melted at about 183° (decomp.), the exact m. p. depending upon the rate of rise of temperature. The extra sensitivity conferred upon a plate on bathing was identical with that given by the dye prepared by the other method.

1 : 6 : 1′ : 6′-*Tetramethyl-ψ-cyanine Iodide*.—The compound prepared by condensation of 2-iodo-6-methylquinoline methiodide and 2 : 6-dimethylquinoline methiodide, in absolute alcoholic solution, was obtained after recrystallisation from spirit in 23% yield. It forms small, dark crystals with a green reflex, m. p. about 250° (decomp.) (Found: I, 27·8. $C_{23}H_{23}N_2I$ requires I, 27·9%). On bathing a plate in its solution, there results a practically uniform band with a very slight minimum at λ 5300 and a maximum at λ 5500, from which the sensitivity gradually decreases to zero at λ 6300; in the emulsion, the sensitivity is extremely feeble, with a decrease in the blue sensitivity. The absorption curves of this and

the preceding ψ-cyanines, in spirit solution, are all very similar. They are characterised by two bands, with maxima at λ 4900 and λ 5220, *respectively*, and the latter of these is the stronger.

1 : 1'-*Diethyl-ψ-cyanine Iodide*.—By the action of potassium hydroxide on an aqueous solution of 2-iodoquinoline ethiodide and quinaldine ethiodide, followed by recrystallisation of the crude dye from methyl alcohol, there resulted an 18% yield, as small, bluish-red crystals, m. p. 277° (decomp.) (Found: I, 28·1. $C_{23}H_{23}N_2I$ requires I, 27·9%). By carrying out the condensation in dry spirit, the yield was 36% (Found: I, 28·0%). The sensitivity curve of a bathed plate shows a gap with its minimum at λ 5300; it then rises to a strong maximum at λ 5700 and falls sharply to zero at λ 6000. In the emulsion, the sensitisation is somewhat less powerful. There is a strong absorption maximum at λ 5250 and a weaker one at λ 4900.

6 (or 6')-*Methyl*-1 : 1'-*diethyl-ψ-cyanine Iodide*.—2-Iodoquinoline ethiodide and 2 : 6-dimethylquinoline ethiodide, condensed in absolute alcoholic solution, gave a 31% yield of the ψ-cyanine, after recrystallisation from methyl alcohol. It forms red needles, m. p. 258° (decomp.) (Found: I, 27·0. $C_{24}H_{25}N_2I$ requires I, 27·1%). With a bathed plate, there is a sensitivity maximum at λ 5800, falling off steeply towards the red. The gap between this crest and the band of ordinary sensitivity has its lowest point at λ 5300. The chief absorption band shows a maximum at λ 5300 and the weaker band a maximum at λ 4950.

1 : 1'-*Diethyl*-5 : 6 (or 5' : 6')-*benz-ψ-cyanine Iodide*.—The condensation of β-naphthaquinaldine ethiodide with 2-iodoquinoline ethiodide is best effected in aqueous solution, giving, after recrystallisation from spirit, a 26% yield of dye, as minute dark green crystals, m. p. 273° (decomp.) (Found: I, 25·2. $C_{27}H_{25}N_2I$ requires I, 25·2%). A plate bathed in its solution is deeply stained; the extra sensitivity is less strong than the blue sensitivity, there is a gap with its minimum at λ 5300 and a maximum at λ 5750, the sensitisation extending to λ 6100 for moderate exposures. In the emulsion, both the ordinary and the extra sensitivity are less and the maximum lies at λ 5850. The absorption maxima are at λ 5000 and λ 5380, the latter being the stronger.

1 : 1'-*Dimethyl*-5 : 6 (or 5' : 6')-*benz-ψ-cyanine Iodide*.—β-Naphthaquinaldine methiodide was condensed with 2-iodoquinoline methiodide in aqueous solution, and the product was washed with boiling water in order to remove unchanged β-naphthaquinaldine methiodide and was then recrystallised from methyl alcohol: a dark, crystalline powder was obtained in 15% yield, m. p. about 266° (decomp.) (Found: I, 26·5. $C_{25}H_{21}N_2I$ requires I, 26·65%).

The sensitising action of a bathed plate extends to λ 6300 for moderate exposures and the maximum lies at λ 5700. The absorption is like that of the preceding compound.

1 : 1′-*Dimethyl*iso*cyanine Iodide*.—The *iso*cyanine was obtained by the action of potassium hydroxide (0·8 g.), dissolved in absolute alcohol (10 c.c.), on a boiling mixture of absolute alcohol (100 c.c.), lepidine methiodide (2 g.; 1 mol.), and 2-iodoquinoline methiodide (2·8 g.; 1 mol.), and the yield after recrystallisation was 34% of that theoretically possible (Found: I, 29·9. Calc. for $C_{21}H_{19}N_2I$: I, 29·8%). The dye was identical in appearance with 1 : 1′-dimethyl*iso*cyanine iodide prepared in the usual way from quinoline methiodide and quinaldine methiodide. Both specimens, and their mixture, possessed the same m. p., and solutions of both showed an identical absorption and imparted the same extra sensitivity to a plate on bathing.

1 : 1′-*Diethyl*iso*cyanine Iodide*.—Condensation of lepidine ethiodide with 2-iodoquinoline ethiodide was carried out similarly and the recrystallised dye was obtained in 45% yield; the yield was only half as great when the condensation was effected in aqueous solution (Found: I, 27·9. Calc. for $C_{23}H_{23}N_2I$: I, 27·9%). The dye was identical in appearance, absorption, and sensitising action on a plate on bathing, with a specimen of 1 : 1′-diethyl*iso*cyanine iodide prepared from quinoline ethiodide and quinaldine ethiodide, and the m. p.'s and mixed m. p. were also the same.

1′ : 2-*Diethylthio-ψ-cyanine Iodide*.—The compound is obtained, in 31% yield, by adding potassium hydroxide (0·7 g.; more than 2 mols.), dissolved in absolute alcohol (10 c.c.), to a hot mixture of absolute alcohol (100 c.c.), 2-iodoquinoline ethiodide (2 g.; 1 mol.), and 1-methylbenzthiazole ethiodide (1·5 g.; 1 mol.), boiling for ½ hour, and recrystallising the product from spirit; it separates as scarlet needles, m. p. 285° (decomp.), as recorded by Mills and Braunholtz (*loc. cit.*) (Found: I, 27·3. Calc. for $C_{21}H_{21}N_2IS$: I, 27·6%). With a bathed plate, the sensitising band is almost uniform, with a maximum at λ 5300 and a very slight depression at λ 5000, the sensitisation extending to λ 5600; in the emulsion, the extra sensitivity is distinctly weaker than the blue sensitivity and the depression is more marked.

1′ : 2-*Dimethylthio-ψ-cyanine Iodide*.—This dye, prepared from 2-iodoquinoline methiodide and 1-methylbenzthiazole methiodide was obtained, after recrystallisation from rectified spirit, in 38% yield; the red crystals show m. p. about 272—276° (decomp.) (Found: I, 29·5. $C_{19}H_{17}N_2IS$ requires I, 29·4%). A plate bathed in its solution shows a uniform sensitisation band extending to λ 5300, falling to a minimum at λ 5700, rising again to a maximum

at λ 6000, and decreasing to zero at λ 6400; but in the emulsion there is practically no extra sensitivity.

1'-Methyl-2-ethylthio-ψ-cyanine Iodide.—The compound was prepared from 2-iodoquinoline methiodide and 1-methylbenzthiazole ethiodide and, after recrystallisation from spirit, resulted in 45% yield. It forms small scarlet crystals, m. p. about 266° (decomp.) (Found: I, 28·5. $C_{20}H_{19}N_2IS$ requires I, 28·5%). When the dye is added to the emulsion, there is a strong sensitising band with its maximum at λ 5300 and a weaker one with its crest at λ 5800.

2-Methyl-1'-ethylthio-ψ-cyanine Iodide.—This dye was similarly prepared from 2-iodoquinoline ethiodide and 1-methylbenzthiazole methiodide. It crystallises from spirit, in 36% yield, as red needles, m. p. about 261—264° (decomp.) (Found: I, 28·7. $C_{20}H_{19}N_2IS$ requires I, 28·45%). The sensitivity of a bathed plate is extended to λ 5350 as a uniform band, which then decreases, but rises to a small crest at λ 5900. With addition of the dye to the emulsion there is a distinct gap between the ordinary and the extra sensitivity, so that a maximum becomes visible at λ 5300; the curve then falls off steeply to a minimum at λ 5600, but rises again to a small crest at λ 5800. The absorptions of this and the three preceding thio-ψ-cyanines are very similar: in each case there is a strong absorption band with its maximum at λ 4850 and a very feeble maximum at λ 4600.

1 : 3 : 3 : *1'-Tetramethylindo-ψ-cyanine Iodide.*—2-Iodoquinoline methiodide (2 g.; 1 mol.), 2 : 3 : 3-trimethylindolenine methiodide (1·5 g.; 1 mol.), and absolute alcohol (10 c.c.) were treated with potassium hydroxide (0·7 g.; more than 2 mols.) dissolved in absolute alcohol (10 c.c.), and the mixture was boiled for 2 hours. The alcohol was evaporated off, water added, and the precipitated solid extracted with ether. The undissolved residue was recrystallised from methyl alcohol; the dye was then obtained, in 26% yield, as brick-red, lustrous crystals, m. p. 247° (decomp.) (Found: I, 28·8. $C_{22}H_{23}N_2I$ requires I, 28·7%). Whether the compound is added to the emulsion before coating or whether a plate is bathed in its solution, there is an extremely feeble extension of the sensitivity to λ 5800, accompanied by a decrease in the ordinary sensitivity. The broad absorption curve shows a maximum at λ 4700.

3 : *3-Dimethyl-1 : 1'-diethylindo-ψ-cyanine Iodide.*—This was similarly prepared from 2-iodoquinoline ethiodide and 2 : 3 : 3-trimethylindolenine ethiodide. After removal of the alcohol from the reaction mixture, the residue was ground with benzene and water, the solid purified by extraction with ether, and the undissolved residue recrystallised from water: a 22% yield resulted, in the form of brown crystals with a green lustre, m. p. about 222° (decomp.)

(Found : I, 26·8. $C_{24}H_{27}N_2I$ requires I, 27·0%). By bathing a plate in a solution of the dye, or by adding the latter to the emulsion, a feeble sensitisation is imparted, extending to λ 5800, and there is a weak maximum at λ 5250. The symmetrical absorption curve has a maximum at λ 4800.

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ILFORD, E. [*Received, December 2nd*, 1927.]

XXXII.—*The Reaction between Diaryloxy*iso*propyl Alcohols and Phosphorus Oxychloride in the Presence of Pyridine.*

By DAVID RUNCIMAN BOYD and DONALD ERNEST LADHAMS.

αγ-DIARYLOXY*iso*PROPYL alcohols react slowly with phosphorus oxychloride at 100°, and from the reaction product, on treatment with ice, a mixture of mono- and bis-esters of phosphoric acid is obtained. A much more rapid reaction takes place, even at low temperatures, when pyridine is employed as solvent and condensing agent.

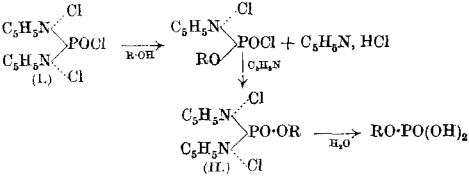
Pyridine has been used by several investigators in the preparation of the esters of inorganic acids. Verley (*Bull. Soc. chim.*, 1901, 25, 46) prepared a series of aryl hydrogen sulphates by means of pyridine and chlorosulphonic acid. These two substances react to give pyridiniumsulphonic acid (Baumgarten, *Ber.*, 1926, **59**, 1166), and this compound has recently been used by Lapworth and Burkhardt for the same purpose (J., 1926, 684) :

$$C_5H_5N\langle{}^{SO_2}_{O}\rangle + R{\cdot}OH \longrightarrow RO{\cdot}SO_2{\cdot}OH.$$

E. Fischer (*Ber.*, 1914, **47**, 3194) introduced the use of pyridine with phosphorus oxychloride for the preparation of phosphoric esters, and the method was afterwards employed by Abderhalden (*Ber.*, 1918, **51**, 1308). Neither investigator has noted that a crystalline compound of pyridine and phosphorus oxychloride is formed when the two liquids are mixed. The analytical data for this substance, although not decisive, point to the formula $(C_5H_5N)_2,POCl_3$. A number of acyl-pyridinium salts are mentioned in the literature; only in a few cases, however, have they been prepared in analytically pure condition. In those compounds which are derived from the chlorides of monobasic acids one molecule of base is associated with one molecule of acyl chloride, but from sulphuryl chloride and pyridine an addition compound has been obtained which probably

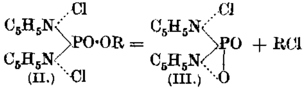
has the formula $(C_5H_5N)_2,SO_2Cl_2$ (Baumgarten, *Ber.*, 1927, **60**, 1174).

Since, in the presence of pyridine, $\alpha\gamma$-diaryloxy*iso*propyl alcohols react with phosphorus oxychloride at 0° and in less than a fifth of the time that is required when no pyridine is present, it is difficult to suppose that the function of the pyridine is merely to fix the hydrogen chloride which is liberated. The pyridine–phosphorus oxychloride addition compound is, doubtless, the reactant:



(1)

Excellent yields of $\alpha\gamma$-diaryloxy*iso*propyl phosphoric esters can be obtained by the pyridine method provided the experimental conditions are suitably regulated. But the unexpected observation has been made that no monophosphoric ester is formed if the reaction mixture, containing excess of phosphorus oxychloride, is heated *in a water-bath for a short time.* The product under these conditions consists mainly of the diaryloxy*iso*propyl chloride, accompanied *by a comparatively small amount of the corresponding* pyridinium compound, which in certain cases can be isolated as the difficultly soluble nitrate. Diaryloxy*iso*propyl alcohols do not yield chlorides on heating with phosphorus oxychloride alone. The presence of pyridine is a necessary factor in the formation of the chloride, and the reaction is most simply explained by assuming a decomposition of the pyridinium compound (II) under the influence of a rise of temperature:



(2)

Phosphorus oxychloride has hitherto been regarded as essentially an agent for the introduction of the phosphoric acid radical. Bergmann in editing a paper by Fischer and Pfähler (*Ber.*, 1920, **53**, 1607) directed attention to the formation of $CH_2Cl{\cdot}CH_2{\cdot}O{\cdot}PO(OH)_2$ from glycol, pyridine, and phosphorus oxychloride as a noteworthy exception to the general rule. Our experiments show, however

that phosphorus oxychloride in association with pyridine may, according to the experimental conditions, act either as a reagent for the introduction of the phosphoric acid radical or for the exchange of hydroxyl for chlorine. The experiments of Fischer and Pfähler were carried out at $-20°$, and their results are interesting as *showing that reaction* (2) *may in some cases occur at low* temperatures.

The formation of an alkylpyridinium compound (*e.g.*, αγ-di-*p*-tolyloxy*iso*propylpyridinium chloride) along with the alkyl chloride requires explanation. The most obvious hypothesis is that two consecutive reactions occur, the pyridinium salt being formed by the combination of pyridine, always present in excess, with some of the alkyl chloride produced in reaction (2). But if this were so, the yield of pyridinium salt ought to be increased by prolonged heating of the reaction mixture. Actually, the yields of chloride and pyridinium salt are constant and unaffected by an increase in the time of heating. Moreover, direct experiment has shown that αγ-di-*p*-tolyloxy*iso*propyl chloride does not form a pyridinium salt on heating with pyridine, even in the presence of phosphorus oxychloride. It would seem, therefore, that the alkylpyridinium salt must be formed by a decomposition of the pyridinium compound (II) proceeding concurrently with the reaction indicated in equation (2):

$$\underset{\text{(II.)}}{\begin{array}{l} C_5H_5N\langle^{Cl} \\ \quad\quad\quad >PO\cdot OR \\ C_5H_5N\langle_{Cl} \end{array}} = C_5H_5N\langle^{R}_{Cl} + C_5H_5N\langle^{POCl}_{O} \quad . \quad . \quad (3)$$

Reaction (2) is closely analogous to the spontaneous decomposition of the unstable addition compounds which pyridine forms with ethyl chloroformate (Fry, *J. Amer. Chem. Soc.*, 1914, **36**, 259) and ethyl chlorosulphonate (Baumgarten, *Ber.*, 1926, **59**, 1166):

$$C_5H_5N + Cl\cdot CO\cdot OEt = C_5H_5N\langle^{CO\cdot OEt}_{Cl} = C_5H_5N + CO_2 + EtCl.$$

$$C_5H_5N + SO_2Cl\cdot OEt = C_5H_5N\langle^{SO_2\cdot OEt}_{Cl} = C_5H_5N\langle^{SO_2}_{O} + EtCl.$$

Reaction (3) is novel in type. It offers a method for the preparation of pyridinium compounds in cases where other processes may be inapplicable or less convenient, and experiments are now in progress to ascertain to what extent it is of general application.

αγ-Di-*p*-tolyloxy*iso*propylpyridinium nitrate may be crystallised from hot water, and is quite stable towards hot dilute acid. It is

decomposed by cold aqueous alkali into *p*-cresol and products which quickly resinify. The splitting off of *p*-cresol under such mild conditions of hydrolysis is remarkable, in view of the great stability of the diaryloxy*iso*propyl alcohols towards hydrolysing agents.

EXPERIMENTAL.

The Addition Compound of Pyridine and Phosphorus Oxychloride. —12 G. of pyridine (3 mols.), dissolved in 40 c.c. of dry ether, were added slowly to a solution of 10 g. of phosphorus oxychloride (1 mol.) in about 40 c.c. of ether, atmospheric moisture being excluded as far as possible. The oily precipitate produced quickly crystallised and was then repeatedly washed, by decantation, with dry ether and dried in a current of dry air for some hours; the last trace of ether was removed under diminished pressure. The product (7·4 g.) was dissolved in water, and the solution made up to a definite volume [Found: P, 9·2; Cl, 27·8. $(C_5H_5N)_2,POCl_3$ requires P, 9·9; Cl, 34·1%].

The compound is extremely hygroscopic and very rapidly decomposed by water. The analytical data may be interpreted as indicating that, in spite of the precautions taken to exclude moisture, a part of the substance has been hydrolysed to the compound (III). The pyridine–phosphorus oxychloride compound dissolves readily in chloroform; it is not soluble in carbon tetrachloride.

Preparation of Phosphoric Esters by the Action of Phosphorus Oxychloride and Pyridine.—The method of procedure, and the general properties of the products are exemplified by the case of di-*p*-tolyloxy*iso*propyl alcohol.

*αγ-Di-*p*-tolyloxyisopropyl phosphate*, $(C_7H_7\cdot O\cdot CH_2)_2CH\cdot O\cdot PO(OH)_2$. In order to obtain a good yield of the mono-ester, it is necessary to use a considerable excess of phosphorus oxychloride. The pyridine–phosphorus oxychloride compound, however, is only slightly soluble in pyridine. Its effective concentration is therefore diminished by separation in solid form, and hence the production of the bis-ester is favoured. This difficulty may be obviated by using a mixture of chloroform and pyridine as the solvent.

A solution of the alcohol (2·72 g.) in 8 c.c. of pyridine was added, in the course of about 20 minutes, to a solution of 3·6 c.c. of phosphorus oxychloride (4 mols.) in 8 c.c. of pyridine (10 mols.), which had been mixed with 10 c.c. of chloroform. The process was carried out in the absence of atmospheric moisture and at 0°. Each drop caused the appearance of a transient red coloration, and towards the end of the operation a small quantity of crystalline matter separated. After standing a short time in ice and for ½ hour at room temperature, the mixture was decomposed with ice and rendered alkaline

with ammonia. The aqueous layer was filtered from the oily mixture of bis-ester and chloroform and made strongly acid. The emulsion which at first formed soon crystallised to a mass of needles, which, after being washed with dilute hydrochloric acid and dried in a vacuum, weighed 3·99 g. (96%). The crystals melted at 158° after recrystallisation from ethyl acetate–light petroleum (Found : P, 8·6. $C_{17}H_{21}O_6P$ requires P, 8·8%).

Di-p-*tolyloxyisopropyl phosphate* is soluble in alcohol, ether, and other organic solvents. It is moderately easily soluble in hot water, and readily soluble in dilute ammonia; more concentrated ammoniacal solutions are soapy and, on evaporation, deposit the *ammonium* salt in oily form. The ester is hydrolysed by warming with hydrochloric acid in aqueous-alcoholic solution; but the sodium salt of the ester is unaffected by boiling with aqueous caustic soda.

Bis-$\alpha\gamma$-*di*-p-*tolyloxyisopropyl phosphate*,

$$[(C_7H_7\cdot O\cdot CH_2)_2CH\cdot O]_2PO\cdot OH.$$

Phosphorus oxychloride was added slowly to an ice-cold solution of the alcohol (1 mol.) in pyridine, the precautions indicated above being taken; the mixture was then heated for about ½ hour in a water-bath. After treatment with ice and ammonia, the pyridine was driven off by heating in the water-bath, and the bis-ester was removed by extraction with ether. The ethereal solution on standing over anhydrous potassium carbonate deposited the potassium salt of the bis-ester, from which the free ester was obtained by treatment with dilute acid. The ester forms needles, m. p. 160°, from acetic acid (Found : P, 4·9. $C_{34}H_{39}O_8P$ requires P, 5·1%). The yield varied considerably. In one experiment it amounted to 94%. When the reaction mixture was not heated before being decomposed with ice, only 20—30% of bis-ester was obtained. The ester is insoluble in water or aqueous caustic alkali. No hydrolysis occurred on boiling a solution of the sodium salt in alcoholic sodium hydroxide.

On evaporating the ethereal solution from which the potassium salt of the bis-ester had separated, there was always obtained a certain amount of a solid substance containing phosphorus, presumably the tri-ester. After recrystallisation from aqueous alcohol it melted at 205—207°. Di-*p*-tolyloxy*iso*propyl chloride is present along with this product if the reaction mixture has been heated before treatment with ice.

$\alpha\gamma$-*Diphenoxyisopropyl phosphate*, $(C_6H_5\cdot O\cdot CH_2)_2CH\cdot O\cdot PO(OH)_2$, m. p. 137—137·5°, crystallises with difficulty. The best solvent is ethyl acetate–light petroleum. The *sodium* salt forms colourless prisms, m. p. 54° (Found : H_2O, 33·0. $C_{15}H_{15}O_6PNa_2,10H_2O$

requires H_2O, 32·8%. Found for the salt dried at 110°: Na, 12·1; P, 8·5. $C_{15}H_{15}O_6PNa_2$ requires Na, 12·5; P, 8·4%).

Bis-αγ-diphenoxyisopropyl phosphate,

$$[(C_6H_5{\cdot}O{\cdot}CH_2)_2CH{\cdot}O]_2PO{\cdot}OH,$$

forms needles, m. p. 105° from acetic acid (Found: C, 65·4; H, 5·8; P, 5·7. $C_{30}H_{31}O_8P$ requires C, 65·4; H, 5·7; P, 5·6%).

αγ-Di-o-tolyloxyisopropyl phosphate, $(C_7H_7{\cdot}O{\cdot}CH_2)_2CH{\cdot}O{\cdot}PO(OH)_2$, could not be crystallised, but its solution in warm aqueous sodium hydroxide gave colourless needles of the *sodium* salt,

$$(C_7H_7{\cdot}O{\cdot}CH_2)_2CH{\cdot}O{\cdot}PO(ONa)_2,10H_2O$$

(Found: P, 5·35; H_2O, 32·9. $C_{17}H_{19}O_6PNa_2,10H_2O$ requires P, 5·4; H_2O, 31·25%).

Preparation of Diaryloxyisopropyl Chlorides and Pyridinium Salts by the Action of Phosphorus Oxychloride and Pyridine.—Di-*p*-tolyloxy-*iso*propyl alcohol was caused to react with phosphorus oxychloride in pyridine solution according to the method described under the preparation of the monophosphoric ester (the use of chloroform as a solvent is not essential). The reaction mixture was then heated in a water-bath for ½ hour. On treatment with ice, αγ-di-*p*-tolyloxy-*iso*propyl chloride separated in almost pure condition; m. p. 73° after crystallisation from alcohol. The yield, 77%, was not altered by keeping the reaction mixture at room temperature for ½ hour before heating or by continuing the heating in the water-bath for an additional 3 hours.

1-*αγ-Di-*p*-tolyloxyisopropylpyridinium nitrate*,

$$C_5H_5N{\cdot}CH(CH_2{\cdot}O{\cdot}C_7H_7)_2,NO_3.$$

The filtrate from the di-*p*-tolyloxy*iso*propyl chloride (about 200—300 c.c.) was mixed with a large excess of saturated ammonium nitrate solution. The *pyridinium nitrate* thus slowly precipitated (yield, 16%) recrystallised from alcohol or chloroform in colourless plates, m. p. 165° (decomp.) (Found: C, 66·6; H, 6·05; N, 7·1. $C_{22}H_{24}O_5N_2$ requires C, 66·7; H, 6·1; N, 7·1%). The corresponding *chlorate*, prepared from the nitrate and potassium chlorate in hot concentrated aqueous solution, crystallised from chloroform in colourless plates, m. p. 153° (violent decomp.) (Found: N, 3·2; Cl, 8·4. $C_{22}H_{24}O_5NCl$ requires N, 3·35; Cl, 8·5%). The thiocyanate, also, is crystalline and sparingly soluble in water. The double compound which the pyridinium chloride forms with mercuric chloride is sticky.

Di-*p*-tolyloxy*iso*propylpyridinium nitrate is decomposed by cold aqueous sodium hydroxide, giving a turbid, brown solution. An alkaline vapour with a peculiar smell is liberated on heating, but no pyridine could be detected. If the resinous matter formed by the action of cold caustic soda is removed by shaking with ether,

cresol can be detected in the colourless alkaline solution. From 8 g. of the pyridinium salt, treated in this manner, 0·43 g. of *p*-tolyl enzoate was obtained, m. p. 69·5° (mixed m. p. 69°). One of the roducts of the alkaline fission of the pyridinium nitrate condenses ith aniline. A solution of the salt in alcohol, containing aniline mol.) and potassium hydroxide (1 mol.), was kept at 0° for 12 ours. Potassium nitrate was deposited, and from the filtrate on eatment with dilute nitric acid deep red crystals were obtained, ı. p. 117—119° (decomp.). The phenomena are similar to those bserved by Zincke in the case of the pyridinium salt derived from initrochlorobenzene (*Annalen*, 1904, **333**, 296). Pyridine, along ith much tarry matter, was obtained on heating the pyridinium itrate with a 10% aqueous solution of sodium acetate for 4 hours t 160°.

1-*αγ-Di*-o-*tolyloxy*iso*propylpyridinium nitrate* forms colourless eaflets, m. p. 154°, from aqueous alcohol. The yield was 12·5% Found: C, 66·5; H, 6·2; N, 7·0%). The properties of the substance are very similar to those of the *p*-tolyl compound.

1-*αγ-Di*-p-*nitrophenoxy*iso*propylpyridinium nitrate* was obtained as olourless prisms, m. p. 182°. It is considerably less stable than the olyl derivatives.

αγ-Di-p-*nitrophenoxy*iso*propyl chloride* is very sparingly soluble in most solvents; it crystallises from glacial acetic acid in prisms, ı. p. 186°. The yield was 84% (Found: Cl, 9·7. $C_{15}H_{13}O_6N_2Cl$ equires Cl, 10·1%).

*The Action of Phosphorus Oxychloride and Pyridine on Diphenoxy*iso*propyl Alcohol at* 100°.—No pyridinium nitrate was isolated in his case; the failure is probably due to the salt being more soluble han the corresponding tolyl compounds. Diphenoxy*iso*propyl hloride was formed in about 75% yield, and no phosphoric esters vere obtained.

*The Action of Phosphorus Oxychloride on Diaryloxy*iso*propyl Alcohols in the Absence of Pyridine.*—This action was investigated n this laboratory some years ago by Mr. A. G. King. Mono- and is-esters of phosphoric acid were obtained from diphenoxy*iso*propyl alcohol and from di-*p*-tolyloxy*iso*propyl alcohol; but in either case could any diaryloxy*iso*propyl chloride be detected.

One of us (D. E. L.) was in receipt of a grant from the Department of Scientific and Industrial Research for a part of the time uring which this investigation was in progress, and grateful acknowledgment of this assistance is made.

UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, November 19th, 1927.*]

XXXIII.—*The Co-ordination Valency of Aluminium in its Salicylato-derivatives.*

By George Joseph Burrows and Ian William Wark.

Various complex aluminium compounds have been described in the literature. In some, the co-ordination number of aluminium is 4, as in $Na[AlCl_4]$ and the alkali aluminates generally, which Heyrovský (J., 1920, **117**, 1013) concluded were derivatives of $H[Al(OH)_4]$. In others, it is 6, as in cryolite. Various aluminium compounds containing residues of organic acids have been described, *viz.*, three types of oxalato-derivatives (all prepared from aluminium hydroxide): $R[Al(C_2O_4)_2]$, $R_2[Al(C_2O_4)_2(OH)]$, and $R_3[Al(C_2O_4)_3]$* (Rosenheim, *Z. anorg. Chem.*, 1896, **11**, 189); aluminium salts of various organic acids, in particular aluminium hydrogen tartrate, $Al(C_4H_5O_6)_3$, and sodium aluminotartrate, $Na_6[Al(C_4H_3O_6)_3]$ (Goldman, *Biochem. Z.*, 1922, **133**, 459); compounds with pyrocatechol to which are assigned formulæ such as $[Al(C_6H_4O_2)_3]K_2H$, $[Al(C_6H_4O_2)_2]K,C_6H_4(OH)_2,2C_2H_4O_2,9H_2O$ (Weinland and Benzel, *Ber.*, 1914, **47**, 2753).

A study of other complex aluminium compounds seemed desirable for various reasons. Aluminium oxide apparently gives rise to two stable hydroxides with 1 and $3H_2O$, respectively, which may be regarded as $H[Al(OH)_4]$ and $H_3[Al(OH)_6]$. The first would conform to the low atomic number of the metal and to its position in the periodic table, from which one might expect co-ordination compounds resembling those of boron, whilst in the second aluminium shows its resemblance to iron and chromium, and this resemblance is further exemplified by the ease of preparation and stability of the normal oxalato-derivatives, $R_3[Al(C_2O_4)_3]$, which are isomorphous with the corresponding ferri- and chrom-oxalates. This work was therefore undertaken with the view of ascertaining whether in its salicylato-derivatives aluminium resembles chromium and iron, or boron.

Furthermore, at the time this investigation was commenced it was hoped that some asymmetric aluminium compounds would be isolated which could be resolved into optical antipodes; but such a resolution has now been effected by Wahl (*Ber.*, 1927, **60**, 399).

Weinland and Zimmermann (*Arch. Pharm.*, 1917, **255**, 204) have studied the iron salicylato-compounds, and Barbieri (*Atti R. Accad. Lincei*, 1915, **24**, i, 605) has prepared various chromium compounds.

* In all our attempts to prepare compounds of these three types from aluminium hydroxide we have succeeded in isolating only compounds of the type $R_3[Al(C_2O_4)_3]$. The oxalato-compounds will be discussed in a subsequent communication.

The latter are of particular interest, since chromisalicylic acid is $H[Cr(C_7H_4O_3)_2],3H_2O$ and salts of the type $R[Cr\{(C_7H_4O_3),NH_3\}_2$ were obtained, in which R is an alkali metal. In both these cases the ratio of chromium to salicylic acid is 1 : 2, and the complex ion is accordingly univalent.

The borosalicylates have been shown by Böeseken and his co-workers to be derivatives of $H[B(C_7H_4O_3)_2]$; and by obtaining the *d*- and *l*-strychnine salts, Böeseken and Meulenhoff (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 174) have definitely established the stereochemistry of these compounds.

It was expected that aluminium compounds would be obtained corresponding to one or other of the acids $H[Al(C_7H_4O_3)_2]$ and $H_3[Al(C_7H_4O_3)_3]$. Our endeavours to prepare these compounds, however, were unsuccessful, and although we obtained evidence of the existence of the compound $Na_3[Al(C_7H_4O_3)_3]$ and the corresponding ammonium salt, we failed to isolate either in a pure condition. The salts isolated all contain sodium (or its equivalent), aluminium, and salicylic acid in the ratio 2 : 1 : 2, together with solvent of crystallisation. *Aluminosalicylic acid*, obtained from neutral solutions of alum and sodium or ammonium salicylate, on drying in a vacuum has the composition $HAl(C_7H_4O_3)_2,2H_2O$, differing from the chromisalicylic acid of Barbieri (*loc. cit.*) in containing $2H_2O$ instead of $3H_2O$. This would suggest the formula $H[Al(C_7H_4O_3)_2],2H_2O$, corresponding to the ordinary valency of aluminium, and a co-ordination number of 4. Experiment showed, however, that this acid requires 2 equivalents of sodium hydroxide for complete neutralisation (and solution), and this fact, together with the nature of the salt so formed and the effect of drying, leads to the conclusion that the acid is dibasic. This can be reconciled with the valency of aluminium by regarding the acid as $H_2\left[Al(C_7H_4O_3)_2{OH \atop OH_2}\right]$, in which the co-ordination valency of aluminium is 6. Derivatives of this acid were prepared (*a*) by neutralising the free acid with the desired base, (*b*) by treating salicylic acid with freshly precipitated aluminium hydroxide and adding the calculated amount of the base, and (*c*) by double decomposition. In all cases the ratio metal (univalent) : aluminium : salicylic acid was 2 : 1 : 2.

Attempts to replace the hydroxyl and the aquo-group by another molecule of salicylic acid, or to introduce another atom of sodium into the molecule, were unsuccessful. No compound of the type $R_3[Al(C_7H_4O_3)_3]$ or $R[Al(C_7H_4O_3)_2]$ could be isolated from aluminium hydroxide and salicylic acid or alkali salicylates.

This result may possibly be due to the formation of the ion

$[Al(C_7H_4O_3)_3]'''$ and its subsequent hydrolysis by water. It was therefore decided to prepare analogous compounds in anhydrous alcohol from aluminium methoxide (or ethoxide), salicylic acid and sodium methoxide (or ethoxide). Although the molecular proportions were varied, the salt which separated from solution invariably had the same molecular ratio as before and in addition contained alcohol. These salts could be recrystallised from anhydrous methyl alcohol, in which they dissolved with a noticeable evolution of heat.

The solution of aluminosalicylic acid formed from aluminium methoxide and salicylic acid was strongly fluorescent when cold, a fact which recalls the conclusions of Waterman (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 581) as to the possibility of tautomerism in salicylic acid and its salts.

From an exhaustive analytical study of the *sodium* salt obtained from aluminium methoxide, salicylic acid, and sodium methoxide we are led to the conclusion that salts obtained in this way and those obtained in aqueous solution from aluminium hydroxide are derivatives of the same acid. Thus the *salt* prepared in methyl alcoholic solution is $Na_2\left[Al(C_7H_4O_3)_2{}^{OH}_{OH_2}\right],2CH_3{\cdot}OH$. Variation in the relative amounts of aluminium, salicylic acid, and sodium methoxide was without effect on the composition of the salt which separated from solution.

It is difficult to explain the presence of hydroxyl and aquo groups in compounds prepared in the absence of water. In view of the precautions taken to render our reagents anhydrous, we feel certain that water was not introduced in this manner, and that these groups result from one of the reactions involved in the preparation.

Attempts to prepare from aluminosalicylic acid and weak bases salts conforming to the type $R_3[Al(C_7H_4O_3)_3]$ were also unsuccessful. No definite ammonium or pyridinium salt could be obtained, and the strychnine salt prepared in alcoholic solution was of the same type as the sodium salt.

The reactivity of aluminium alkyloxides towards salicylic acid together with the ease of obtaining pure derivatives by using this material as the starting point, induced us to study the action of ethyl and methyl salicylates on aluminium ethoxide and methoxide respectively. In this way crystalline *products* were obtained the compositions of which are represented by $Al(C_9H_9O_3)_3$ and $Al(C_8H_7O_3)_3$ respectively. In view of the fact that phenol yields a crystalline derivative, it appeared possible that these compounds were simply salts of tervalent aluminium. However, experiment

in which other esters, *e.g.*, ethyl malonate and benzoate, were caused to react with aluminium ethoxide lead to the conclusion that these compounds are co-ordination compounds of aluminium, and that not only is the hydrogen of the phenolic group reactive in this connexion, but that co-ordination also takes place through the ketonic oxygen of the ester. We are thus of the opinion that the constitution of the ester products is correctly represented by the formulæ given, in which the co-ordination valency of aluminium is 6.

The ethyl malonate compound, like the aluminium salicylic esters, was isolated in a crystalline condition, and analysis indicates that it is aluminium malonic ester, $[Al\{CH(CO_2Et)_2\}_3]$, identical with that prepared by Titschenko (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 694, 784); the extraordinary solubility of this compound in liquids of low dielectric constant indicates that it is not an aluminium salt.

The ethyl benzoate compound has not yet been obtained in a crystalline condition sufficiently pure for further investigation.

It is our intention to study the action of certain aldehydes on the aluminium alkyloxides.

EXPERIMENTAL.

Aluminosalicylic Acid, $H_2\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right]$.—(*a*) On mixing hot aqueous solutions of potash alum (1 mol.) and of sodium or ammonium salicylate (2 mols.), a violet-pink solution was obtained from which fine, pink needles gradually separated. The product contained varying amounts of free salicylic acid, which was removed by washing with alcohol. *Aluminosalicylic acid* is only sparingly soluble in water, but on being moistened on litmus paper it gives an acid reaction. The acid requires 2 equivs. of sodium hydroxide for complete solution; further alkali renders the solution alkaline to litmus. On drying in an oven at 100°, the acid readily loses 1 molecule of water, a second being driven off only with difficulty (Found: Al, 7·8. $C_{14}H_{13}O_8Al$ requires Al, 8·0%).

(*b*) The same compound was obtained by mixing hot aqueous solutions of aluminium chloride (1 mol.) and salicylic acid (2 mols.) and washing the crystalline precipitate with alcohol (Found: Al, 7·8%).

(*c*) On adding an aqueous-alcoholic solution of salicylic acid (2 mols.) to a cold suspension of freshly precipitated aluminium hydroxide, the latter dissolved, but a pink crystalline precipitate of aluminosalicylic acid slowly separated (Found: Al, 7·8%).

(*d*) A solution of salicylic acid (2 mols.) in anhydrous alcohol (dehydrated with metallic calcium or aluminium) was added to a suspension of aluminium ethoxide (1 mol.) in anhydrous alcohol.

On warming, a clear purple solution was obtained having a blue fluorescence. No precipitate was formed, but on concentration in a vacuum desiccator, a pink, crystalline product was obtained which was dried over sulphuric acid (Found: Al, 7·9%).

In preparing the aluminium alkyloxides used in this work the procedure was as follows. The alcohol was first dehydrated by refluxing it with fine calcium turnings, or with very fine aluminium foil together with an extremely small quantity of mercuric chloride, and then distilling it, calcium chloride guard tubes being used throughout. A known weight of aluminium foil was then heated under reflux with dry alcohol and a trace of mercuric chloride until the aluminium was completely converted into alkyloxide. (In this operation it was found advantageous to add the alcohol very gradually—the reaction apparently proceeding most rapidly when metallic aluminium is exposed to alcohol vapour.) A solution of salicylic acid in anhydrous alcohol was then added.

Sodium Aluminosalicylate.—(a) *The monohydrate*,

$$Na_2\left[(C_7H_4O_3)_2Al{OH \atop OH_2}\right],H_2O.$$

Aluminosalicylic acid was dissolved in the minimum quantity of aqueous sodium hydroxide. The deep yellow solution was warmed, filtered from excess of the acid (trace), and the filtrate concentrated on the water-bath under diminished pressure. The yellowish-pink needles that separated on cooling were filtered off and washed with alcohol. More of the salt was obtained from the mother-liquor by the addition of alcohol. The salt is extremely soluble in water and fairly readily soluble in methyl alcohol. An aqueous solution is alkaline to litmus (Found: Loss at 120°, 9·0; Al, 6·8; Na, 11·6; $C_7H_4O_3$, 67·2. $C_{14}H_{13}O_9AlNa_2$ requires Al, 6·75; Na, 11·5; $C_7H_4O_3$, 68·0; $2H_2O$, 9·0%).

(b) *The dimethyl-alcoholate*, $Na_2\left[(C_7H_4O_3)_2Al{OH \atop OH_2}\right],2CH_3OH$. A solution of salicylic acid (2 mols.) in anhydrous methyl alcohol was added to aluminium methoxide (1 mol.) in methyl alcohol. On refluxing for some time, a clear solution was obtained, and to this was added a solution of sodium methoxide (2 mols.) in methyl alcohol. On cooling the yellow solution so obtained, the salt separated in cream-coloured needles; it was recrystallised from methyl alcohol and air-dried. In the process of crystallisation from methyl alcohol, the dissolution of the salt was strongly exothermic, and, on cooling, the separation of the salt was remarkably sudden, suggesting the possibility of the process being one of alcoholysis followed by recombination to form the salt. On drying at [illegible]° the salt lost 14·7%, corresponding to 2 molecules of

methyl alcohol. Owing to the difficulty of carrying out combustions with compounds of this type, several analyses were made, both of the air-dried salt and of the salt from which the alcohol had been expelled in the oven. Furthermore, combustions were effected in moist oxygen and also by the "wet" chromic acid method. In every case the results were concordant (Found: C, 43·3; H, 4·6; Al, 6·2; Na, 10·4; $C_7H_4O_3$, 60·6. $C_{16}H_{19}O_{10}AlNa_2$ requires C, 43·3; H, 4·3; Al, 6·1; Na, 10·4; $C_7H_4O_3$, 61·2; 2MeOH, 14·5%). The same salt is apparently obtained by using aluminium ethoxide and sodium ethoxide in place of the corresponding methoxides and recrystallising the product from methyl alcohol (Found: Al, 6·0; Na, 10·2%).

(c) *The dihydrate*, $Na_2\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right],2H_2O$. This salt was obtained from the preceding by dissolving 5 g. in 20 c.c. of water at 40° and adding 100 c.c. of ethyl alcohol. The solution was kept at 40° for 2 hours and then allowed to stand over-night; a copious, cream-coloured, crystalline precipitate thus separated (Found: Al, 6·6; Na, 11·0. $C_{14}H_{15}O_{10}AlNa_2$ requires Al, 6·5; Na, 11·1%).

Barium Aluminosalicylate, $Ba\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right],H_2O$.—This salt was obtained by adding an aqueous solution of sodium aluminosalicylate dihydrate to an aqueous solution of barium chloride, both at 40°. After a few minutes, a cream-coloured, crystalline precipitate separated. After 2 hours, this was removed by filtration and washed with water, in which the salt is only sparingly soluble. On drying in a desiccator over sulphuric acid, there was a slight change in colour, the final product being pale yellow (Found: Al, 5·6; Ba, 27·9. $C_{14}H_{13}O_9AlBa$ requires Al, 5·5; Ba, 28·1%). The same compound was obtained from a solution of sodium aluminosalicylate dimethyl-alcoholate at 40° by addition of barium chloride solution.

Ammonium Aluminosalicylates.—Several attempts were made to prepare definite salts by passing dry ammonia into an alcoholic solution of aluminosalicylic acid prepared from aluminium ethoxide and salicylic acid in ethyl alcohol. Although crystalline products were obtained, these always liberated the free aluminosalicylic acid on attempts at recrystallisation from methyl alcohol, and the analyses of such compounds indicated that the substance which originally separated in the preparation was invariably a mixture of aluminosalicylic acid and ammonium aluminosalicylate.

Strychnine Aluminosalicylate, $C_{21}H_{22}O_2N_2,H\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right]$.—From the composition of the various salts isolated in this work,

we were led to conclude that the constitution of the complex ion is $\left[(C_7H_4O_3)_2Al{}^{OH}_{OH_2}\right]$.

Since the hydroxyl and the aquo-group are obviously in the 1 : 6 positions, such an ion is asymmetric and should be capable of resolution into optical antipodes. So far, we have failed to carry out such a resolution. We have, however, isolated definite crystalline alkaloidal salts such as the strychnine, brucine, quinine, and narcotine compounds. Of these only the strychnine salt was analysed; it was prepared by adding the calculated amount of the alkaloid, dissolved in hot chloroform, to a hot alcoholic solution of aluminosalicylic acid, and cooling the solution. Although the molecular proportion of strychnine was varied, the composition of the salt did not change. Attempts to separate the optical isomerides by fractional crystallisation from alcohol or mixtures of alcohol and chloroform were unsuccessful (Found : Al, 4·0. $C_{35}H_{34}O_{10}N_2Al$ requires Al, 4·0%).

Aluminium Methyl Salicylate, $(C_8H_7O_3)_3Al$.—This compound was obtained by adding freshly distilled methyl salicylate (3 mols.) to an alcoholic solution of aluminium methoxide (1 mol.). The solution became pink, and after refluxing for 2 hours was kept over-night, whereupon well-formed, lustrous, brown crystals separated. These were washed with a small quantity of alcohol and then with ether, and dried in a desiccator. They did not melt sharply on heating, but apparently underwent decomposition (Found : C, 60·0; H, 5·3; Al, 5·6. $C_{24}H_{21}O_9Al$ requires C, 60·0; H, 4·4; Al, 5·6%).

Aluminium Ethyl Salicylate, $(C_9H_9O_3)_3Al$.—This compound was prepared in an analogous manner to the preceding. The crystals obtained were similar in appearance to those of the previous compound (Found : C, 61·1; H, 5·4; Al, 5·0. $C_{27}H_{27}O_9Al$ requires C, 62·1; H, 5·2; Al, 5·2%).

Aluminium Ethyl Malonate, $(C_7H_{11}O_4)_3Al$.—This compound was obtained by Titschenko (*loc. cit.*) by acting on aluminium with ethyl malonate in the presence of a trace of mercuric chloride. In the present work, it was obtained in a manner similar to that adopted for the preparation of the aluminium salicylic esters, *i.e.* by the interaction of ethyl malonate and aluminium ethoxide in the presence of ethyl alcohol. It is readily decomposed by water, and is remarkably soluble in all organic liquids. In fact, we had great difficulty in recrystallising the compound from any solvent and finally had to allow a solution in ether partly to evaporate in order to obtain a pure crystalline product (Found : C, 49·8; H, 6·6; Al, 5·4. Calc. : C, 50·0; H, 6·5; Al, 5·4%).

Summary.

1. Several derivatives of aluminosalicylic acid,

$$H_2\left[(C_7H_4O_3)_2Al^{OH}_{OH_2}\right],$$

have been prepared from aqueous and alcoholic solutions. It has not been possible to prepare alkali-metal derivatives of $H[Al(C_7H_4O_3)_2]$ or of $H_3[Al(C_7H_4O_3)_3]$.

2. An attempt to resolve the strychnine, brucine, quinine, and narcotine salts of the above acid into optical isomerides was unsuccessful.

3. Reactions between aluminium alkyloxides and certain esters, *e.g.*, methyl salicylate and ethyl malonate, produce complexes of the type $Al[(C_8H_7O_3)_3]$ and $[Al\{CH(CO_2Et)_2\}_3]$.

THE UNIVERSITY, SYDNEY. [*Received, December 5th,* 1927.]

XXXIV.—*The Migration of the Acyl Group in Partly Acylated Phenolic Compounds. Part I.*

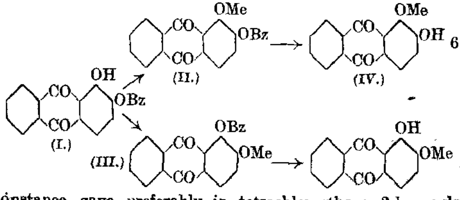
By ARTHUR GEORGE PERKIN and RALPH CHARLES STOREY.

WHEN 2-acetylalizarin is methylated with diazomethane (Kubota and Perkin, J., 1925, **127**, 1889) a wandering of the acetyl group occurs, 1-acetylalizarin 2-methyl ether (6 parts) and 2-acetylalizarin 1-methyl ether (1 part) being obtained. In an analogous manner, 2 : 3-diacetylanthragallol (referred to later) gives 1 : 3-diacetylanthragallol 2-methyl ether and 2 : 3-diacetylanthragallol 1-methyl ether, the former as chief product. When, however, 3 : 7 : 3′ : 4′-tetra-acetylquercetin is treated similarly, migration of the acetyl group does not occur, only 3 : 7 : 3′ : 4′-tetra-acetylquercetin 5-methyl ether being produced. The present investigation was undertaken to study, not only the behaviour of other partly acetylated hydroxy-ketones with diazomethane, but also the effect in these circumstances of the carbethoxy-, benzoyl, and toluene-*p*-sulphonyl groups. It was desirable again to devise a method whereby α-methyl ethers of the hydroxyanthraquinones, only traces of which have been hitherto available, could be obtained in reasonable amount for further study.

The general methods here devised for the preparation of the hitherto unknown partly acylated compounds required for this work, which are described in the sequel, hardly require comment. For the preparation of 2-benzoylalizarin and 2-benzoylanthrapurpurin, however, somewhat novel processes, involving the action of benzoyl chloride in presence of pyridine on 2-acetylalizarin and

2 : 7-diacetylanthrapurpurin, respectively, were employed. In th former case, 1-acetyl-2-benzoylalizarin, and in the latter 2-benzoyl 1 : 7-diacetylanthrapurpurin, was obtained, a migration of a acetyl group from the 1- to the 2-position having occurred in bot cases. From these compounds by acid hydrolysis the desire 2-benzoylalizarin and 2-benzoylanthrapurpurin were obtained Again, 2 : 3-diacetylanthragallol with excess of benzoyl chlorid yielded the 2 : 3-dibenzoyl-1-acetyl compound (a reaction whic involves the migration of one acetyl group and the replacement of second by a benzoyl group); this by removal of the acetyl grou gave the dibenzoylanthragallol required for investigation. I these cases, migration occurs during the benzoylation, and n alteration of the position of the benzoyl group occurs during th subsequent hydrolysis of the benzoylacetyl compound. Thes results thus differ from those observed by Fischer, Bergmann, an Lipschitz (*Ber.*, 1918, **51**, 45), who cite, together with other cases the formation by hydrolysis of 3-benzoylgallic acid from 4-benzoyl 3 : 5-diacetylgallic acid and of 3-benzoylprotocatechuic acid fron 4-benzoyl-3-acetyl-protocatechuic acid.

In the methylation, various solvents—ether, acetone, tetra chloroethane, and nitrobenzene—were employed, dependent i each case on the more ready solubility of the acetyl compoun therein. From isolated experiments, it did not appear that th migration varied appreciably in amount by the use of one or othe of these solvents, or that this could be rendered complete, or wa indeed affected, by the employment of a very large amount of diazo methane. Owing to the formation of viscid matter, the yield o crystalline methylation product which could be isolated varie according to the acyl compound under investigation, and in som cases (compare acetylpurpurin) was poor. The results given below expressed in parts, are the relative quantities of the methyl ether isolated from the reaction product. 2-Benzoylalizarin (I), fo



(I.) (II.) (III.) (IV.) 6 parts 1 part

instance, gave preferably in tetrachloroethane 2-benzoylalizari 6-methyl ether (II) (6 parts) and 1-benzoylalizarin 2-methyl ethe

III) (1 part). From these compounds by hydrolysis, alizarin 1-IV) and 2-methyl ethers were respectively obtained.

In the other results, expressed as follows, the presence of an sterisk indicates that the compound though present was not isolated.

-Ethylcarbonato-alizarin	↗	1-Ethylcarbonato-alizarin 2-methyl ether	→	Alizarin 2-methyl ether (1 part)
	↘	2-Ethylcarbonato-alizarin 1-methyl ether	→	Alizarin 1-methyl ether (3 parts)
-Toluene-*p*-sulphonyl-alizarin	→	2-Toluene-*p*-sulphonyl-alizarin 1-methyl ether	→	Alizarin 1-methyl ether (sole product)
: 7-Diacetylanthra-purpurin	↗	1 : 7-Diacetylanthra-purpurin 2-methyl ether *	→	Anthrapurpurin 2-methyl ether
	↘	2 : 7-Diacetylanthra-purpurin 1-methyl ether *	→	Anthrapurpurin 1-methyl ether
: 7-Diethylcarbonato-anthrapurpurin	↗	1 : 7-Diethylcarbonato-anthrapurpurin 2-methyl ether *	→	Anthrapurpurin 2-methyl ether (2 parts)
	↘	2 : 7-Diethylcarbonato-anthrapurpurin 1-methyl ether	→	Anthrapurpurin 1-methyl ether (5 parts)
-Benzoylanthra-purpurin	↗	1-Benzoylanthra-purpurin 2 : 7-dimethyl ether	→	Anthrapurpurin 2 : 7-dimethyl ether
	↘	2-Benzoylanthra-purpurin 1 : 7-dimethyl ether	→	Anthrapurpurin 1 : 7-dimethyl ether
-Acetylpurpurin	↗	1-Acetylpurpurin 2 : 4-dimethyl ether	→	Purpurin 1 : 3-dimethyl ether (5 parts)
	↘	1-Acetylpurpurin 2-methyl ether	→	Purpurin 2-methyl ether (1 part)
-Acetylpurpuro-xanthin	→	3-Acetylpurpuro-xanthin 1-methyl ether	→	Purpuroxanthin 1-methyl ether (sole product)
1 : 2(or 2 : 3)-Diethyl-carbonatoanthra-gallol	↗	2 : 3(or 1 : 2)-Diethyl-carbonatoanthra-gallol 2-methyl ether	→	Anthragallol 1- or 3-methyl ether
	↘	1 : 3-Diethylcarbon-atoanthragallol 2-methyl ether	→	Anthragallol 2-methyl ether
3 : 4(or 2 : 3)-Diacetyl-gallacetophenone	↗	2 : 4-Diacetylgalláceto-phenone 3-methyl ether	→	Gallacetophenone 3-methyl ether (A)
	↘	3 : 4(or 2 : 3)-Diacetyl-gallacetophenone 2 (or 4)-methyl ether	→	Gallacetophenone 2 (or 4)-methyl ether (B)
3 : 4(or 2 : 3)-Ditolu-ene-*p*-sulphonyl-gallacetophenone	→	3 : 4(or 2 : 3)-Ditolu-ene-*p*-sulphonyl gallacetophenone 2 (or 4)-methyl ether	→	Gallacetophenone 2 (or 4)-methyl ether

In the above experiment with 2-acetylpurpurin, much viscid matter was produced, and therefore it is possible that traces of

2-acetylpurpurin 1-methyl ether were also present, but escaped detection.

The position of the methoxy-groups in these compounds could be deduced from their behaviour with boiling acetic anhydride; for instance, under identical conditions anthrapurpurin 1- and 2-methyl ethers yielded the 2 : 7- and 7-acetyl derivatives, *respectively*.

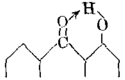
That the *gallacetophenone methyl* ether (A), which is identical with that obtained by one of us (J., 1903, **83**, 131) from mono-potassium gallacetophenone and methyl iodide, contains the methoxy-group in position 3 is evident from its properties and the fact that (by methods described later) it yields pyrogallol 2-methyl ether. (B), on the other hand, which in similar circumstances gives pyrogallol 1-methyl ether, is either the 2- or 4-methyl ether of gallacetophenone, for although analogy suggests that it has the former constitution and that the partly acetylated gallacetophenone from which it is derived is the 3 : 4-acetyl compound, this is hardly certain, because in view of the work of Pascu (*Ber.*, 1923, **56**, 407) on the acetyl derivatives of 2 : 3 : 4-trihydroxybenzoic acid, a possibility exists that this may be the 2 : 3-diacetyl derivative. A similar uncertainty exists in regard to the position of the acetyl groups in the partial acetylation product of anthragallol, which by analogy with alizarin has been hitherto assumed to be the 2 : 3-diacetyl derivative, for there is a possibility as a result of the work of one of us and Mr. C. W. H. Story now in progress, that the acetyl groups may be in the 1 : 2-diacetyl positions and that the product of its methylation, described by Kubota and Perkin (*loc. cit.*) as anthragallol 1-methyl ether, is in reality the 3-methoxy-compound.

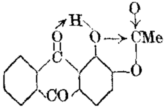
The results of this and the preceding investigation (*loc. cit.*) show that by methylating the hydroxyacetoxyanthraquinones enumerated above with diazomethane the migration of the acetyl group approximates to 85%. When the ethylcarbonato-group is similarly present, this wanders to a less extent (about 25%), and the migration of the benzoyl group is even smaller (about 20%). With the toluene-*p*-sulphonyl group, however, migration does not occur, and as a result a method is now available whereby good yields of the 1 (or 3)-methyl ethers of hydroxyanthraquinones or hydroxyketones can be obtained.

When, as with monoacetylpurpuroxanthin, the acetoxy- and hydroxy-groups are not vicinal, migration of the acetyl group does not occur under the influence of diazomethane, as was also the case with 4 : 7 : 3′ : 4′-tetra-acetylquercetin in similar circumstances (*loc. cit.*). Somewhat analogous are the results of Bergmann and Dangschat (*Ber.*, 1919, **52**, 371), who observed that the migration

of the benzoyl group described by Fischer, Bergmann, and Lipschitz, referred to above, does not take place with similar derivatives of β-resorcylic and gentisic acids. Again, migration of the benzoyl group does not occur when 2-benzoylresorcylic acid is submitted to the action of diazomethane.

Adopting the suggestion of Sidgwick and Callow (J., 1924, **125**, 527; compare Dimroth and Faust, *Ber.*, 1921, **54**, 3126) that the inert character of the α-hydroxyl of hydroxy-ketones in comparison with that in the β-position is to be explained by the presence of a six-membered chelate ring (V), it would appear that, if in such

(V.) 

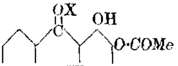
 (VI.)

compounds the attraction of the carbonyl for the 1-hydroxyl was removed, the latter would then possess more " basic " properties, or a greater attraction for the acyl group, than that in the 2-position. Such a view receives some support from the work of Bergmann and Dangschat (*loc. cit.*), who showed that by cautious hydrolysis both diacetyl-β-resorcylic acid and diacetylgentisic acid yielded the 2-acetyl derivative. Again (Pascu, *loc. cit.*), by similar treatment, 4-hydroxy-2 : 3-diacetoxybenzoic acid gives apparently the 3 : 4-dihydroxy-2-acetoxy-compound.

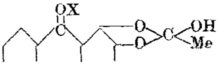
That, on the other hand, the 2-hydroxyl of the hydroxy-ketone dyes has marked " acidic " property is suggested by the fact (Perkin, J., 1899, **75**, 433) that by the action of alcoholic potash, or alcoholic potassium acetate, on these compounds the 2-potassiumoxy-salt is first produced. The 2-hydroxyl is, however, more readily acylated than the 1-hydroxyl, and this apparent anomaly may be due to the fact that the " basic " function of the latter is suppressed, at least in part, by its co-ordination with the carbonyl group. It seems likely that the 2-acetyl group to some extent attracts the 1-hydroxyl, so that the chelate ring is weakened—an effect which may be expressed (VI) by means of a co-ordinate link between the oxygen of the 1-hydroxyl and the acetyl group.

In discussing the migration of the acyl group from the 2- to the 1-position under the influence of diazomethane, the transformation of 2-acetylalizarin into 1-acetylalizarin 2-methyl ether may be taken as typical. Although a trace of 2-acetylalizarin 1-methyl ether is present in the reaction product, there is no reason to presume that this is the initial product of the reaction, from which, by an interchange in the positions of methyl and acetyl, the 1-acetyl-

alizarin 2-methyl ether is formed subsequently. It seems more probable indeed that migration of the acetyl from the 2- to the 1-position first occurs, and that this is followed by the methylation of the 2-hydroxyl thus vacated. For these changes to occur, it is probable that, as a preliminary, the influence of the carbonyl on the 1-hydroxyl has been suppressed or rendered non-existent, and that this, it is suggested, may have arisen from the production of a loose compound of diazomethane with the carbonyl oxygen. The nature of such a combination need not be at present discussed and is here (VII) referred to as X.



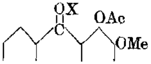
(VII.)

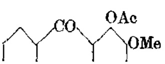


(VIII.)

As a result, the full attraction of the 1-hydroxyl for the acetyl group now comes into play, and migration of the latter from the 2- to the 1-position occurs, possibly *via* some intermediate stage as (VIII), a type of change which has been suggested by Fischer, Bergmann, and Lipschitz (*loc. cit.*) in explanation of the wandering of the benzoyl group in the benzoylhydroxybenzoic acids above referred to. Excess of diazomethane being present, methylation of the 2-hydroxyl (IX) now occurs, and finally, as diazomethane disappears from the solution, the addition product of the latter with the carbonyl group suffers decomposition (X).

(IX.)





(X.)

Should the co-ordinating effect of the carbonyl be concerned with the para- rather than with the α-hydroxyl, as may perhaps be the case in the diacetylanthragallol and diacylgallacetophenones here studied, then the migration of the acyl group which occurs when these compounds are treated with diazomethane can be similarly explained.

Such a theory will also account for the wandering of the acetyl group during benzoylation, as in the formation of 2-benzoyl 1-acetylalizarin from 2-acetylalizarin (*loc. cit.*), it being assumed, in this case, that the formation of a loose compound between the carbonyl and either benzoyl chloride or the catalyst precedes the migration process.

The fact that in similar circumstances the ethylcarbonato- and [illegible]oyl groups wander to a less extent than the acetyl group is [illegible]ly to be accounted for by their higher molecular weight and

lower acidity, and consequent resistance to displacement, whereas the complete lack of migration shown by the strongly acid toluene-*p*-sulphonyl radical can only be explained on the former assumption.

An account of the preparations, from anthragallol, of the anthragallol 1 : 3- and 1 : 2-dimethyl ethers present in Chay Root which has been recently effected by one of us and Mr. C. W. H. Story will be communicated to the Society in due course.

EXPERIMENTAL.

2 : 7-*Diacetylanthrapurpurin*.—Commercial anthrapurpurin purified by the method of Goodall and Perkin (J., 1924, **125**, 473) (5 g.) was digested with a boiling mixture of acetic anhydride (50 c.c.) and acetic acid (50 c.c.). Twenty drops of pyridine were added, and when solution was complete the liquid was poured into alcohol. The deposit, recrystallised from alcohol-acetic acid, gave fine, yellow needles, m. p. 192—193° (Found : C, 63·3 ; H, 3·6. $C_{18}H_{12}O_7$ requires C, 63·5 ; H, 3·55%).

Alternatively, potassium acetate (2·5 g.) was boiled with acetic anhydride (25 c.c.) and, when the mixture was cold, anthrapurpurin (5 g.) was added. The crystals which had separated over-night melted at 192—193° after recrystallisation. The diacetyl compound which is described by Knoll and Co. (D.R.-P. 117730) as melting at 175—178°, and is said to be prepared by the gentle acetylation of anthrapurpurin, can hardly be a pure compound.

Methylation. 2 : 3-Diacetylanthrapurpurin (2 g.) in nitrobenzene (35 c.c.) or acetone (150 c.c.) was treated with ethereal diazomethane from nitrosomethylurethane (9·25 c.c.). After 2 days, the filtered solution was freed from ether and steam-distilled to remove nitrobenzene. The viscid residue was hydrolysed in acetic acid (15 c.c.) with hydrochloric acid in the usual manner, and hot water cautiously added to the solution. When cold, the crystals were collected and fractionally crystallised from alcohol. The sparingly soluble fraction, which formed orange-red needles, m. p. 308—309°, consisted of *anthrapurpurin 2-methyl ether* (Found : C, 66·7 ; H, 4·1 ; CH_3, 5·6. $C_{15}H_{10}O_5$ requires C, 66·7 ; H, 3·7 ; CH_3, 5·55%).

1 : 7-*Diacetylanthrapurpurin 2-methyl ether*, obtained by means of acetic anhydride and pyridine, crystallises in yellow leaflets, m. p. 154—155° (Found : C, 64·1 ; H, 4·0. $C_{19}H_{14}O_7$ requires C, 64·4 ; H, 4·0%). By a short digestion, however, with boiling acetic anhydride in the absence of pyridine, orange-yellow needles, m. p. 207°, of 7-*acetylanthrapurpurin 2-methyl ether* are obtained.

The alcoholic mother-liquor from which the 2-methyl ether had separated was treated with baryta water, to precipitate as barium

salt traces of the latter still present; the mixture was then boiled and filtered, and the filtrate made acid with hydrochloric acid. The crystals which separated were acetylated, for which purpose the use of pyridine was unnecessary, and the 2 : 7-*diacetylanthrapurpurin* 1-*methyl ether* recrystallised first from acetone and then from alcohol. It consisted of pale yellow leaflets, m. p. 136—137° (*Found* : C, 64·2; H, 3·95. $C_{19}H_{14}O_7$ requires C, 64·4; H, 4·0%).

Hydrolysis with hydrochloric acid gave orange-red needles of *anthrapurpurin* 1-*methyl ether*, m. p. 299—300° (Found : $C_{15}H_{10}O_5$, 76·2. Calc., 76·3%. Found : C, 67·0; H, 4·0; CH_3, 5·3. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7; CH_3, 5·5%).

2 : 7-*Diethylcarbonatoanthrapurpurin*.—Anthrapurpurin (2 g.) in pyridine (25 c.c.) was treated drop by drop with ethyl chloroformate (1·8 c.c.), the temperature being kept at about 30°. After 1 hour, water (20 c.c.) was slowly added, and when crystals ceased to separate these were collected and recrystallised from alcohol. The golden-yellow needles melted at 166—167° (Found : C, 60·1; H, 4·25. $C_{20}H_{16}O_9$ requires C, 60·0; H, 4·0%). Yield, 1·43 g.

Methylation. 2 : 7-Diethylcarbonatoanthrapurpurin (2 g.) in tetrachloroethane (30 c.c.) was treated with diazomethane from nitrosomethylurethane (8 c.c.). After 3 days, the filtered solution was steam-distilled, and the viscid residue well dried. A solution of the latter in methyl alcohol (25 c.c.) (charcoal), deposited lemon-yellow needles of pure 2 : 7-*diethylcarbonatoanthrapurpurin* 1-*methyl ether* (0·75 g.), m. p. 120—121° (Found : C, 60·8; H, 4·2. $C_{21}H_{18}O_9$ requires C, 60·9; H, 4·3%).

For hydrolysis, boiling 1% methyl-alcoholic potash was used, and the claret solution was diluted with water and acidified with hydrochloric acid. The yellow needles of anthrapurpurin 1-methyl ether which separated (0·5 g.) melted at 299—300° (Found : C, 66·6; H, 3·8%).

The alcoholic mother-liquors from which the 2 : 7-diethylcarbonatoanthrapurpurin 1-methyl ether had separated were concentrated, and while boiling, treated with a little methyl-alcoholic potash. The diluted solution on acidification deposited orange needles of anthrapurpurin 2-methyl ether (0·2 g.), m. p. 308—309° (Found : C, 66·5; H, 4·1%).

2-*Benzoyl*-1 : 7-*diacetylanthrapurpurin*—To 2 : 3-diacetylanthrapurpurin (1 g.) in chloroform (6 c.c.) and benzoyl chloride (1·3 c.c.), pyridine (1 c.c.) was slowly added, rise of temperature being avoided. After 2 days, the mixture was diluted with alcohol, and the separated product recrystallised from alcohol or acetic acid. The pale yellow plates or leaflets melted at 201—203° (Found : C, 67·7; H, 3·8. $C_{25}H_{16}O_8$ requires C, 67·6; H, 3·6%).

2-*Benzoylanthrapurpurin*.—By cautious hydrolysis of the benzoyl-diacetyl compound, 79·8% of 2-benzoylanthrapurpurin was obtained, (theoretical, 80·5%). The product crystallised from methyl alcohol or tetrachloroethane as yellow plates or prisms, m. p. 272—273° (Found: C, 69·85; H, 3·6. $C_{21}H_{12}O_6$ requires C, 70·0; H, 3·3%). The yield reckoned on the diacetylanthrapurpurin employed was about 20%.

Methylation. A solution of 2-benzoylanthrapurpurin (2 g.) in hot tetrachloroethane (120 c.c.) was cooled, some crystals separating, and the mixture was treated with diazomethane from nitroso-methylurethane (14 c.c.). After 2 days, the filtered solution was steam-distilled, and the viscid residue dissolved in hot methyl alcohol (550 c.c.) (charcoal). The crystals of the sparingly soluble 2-*benzoylanthrapurpurin* 1 : 7-*dimethyl ether* (Filtrate A), by recrystallisation from methyl alcohol, formed lemon-yellow leaflets, m. p. 201—203° (Found: C, 71·1; H, 4·15; CH_3, 7·7. $C_{23}H_{16}O_6$ requires C, 71·1; H, 4·1; CH_3, 7·7%).

For hydrolysis, boiling 2% methyl-alcoholic potash was used, and the solution was diluted with hot water and acidified. Yellow needles of *anthrapurpurin* 1 : 7-*dimethyl ether*, m. p. 218—219°, soluble in dilute alkali with a red colour, thus separated (Found: C, 67·6; H, 4·3. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%).

Acetylation in the absence of pyridine yielded 2-*acetylanthrapurpurin* 1 : 7-*dimethyl ether* as pale yellow needles, m. p. 175—176°.

The methyl-alcoholic filtrate (A) on evaporation to about 50 c.c. gave crystals, which were deposited from alcohol–acetic acid as yellow plates, m. p. 209—211° (Found: C, 70·5; H, 4·1; CH_3, 7·9. $C_{23}H_{16}O_6$ requires C, 71·1; H, 4·1; CH_3, 7·7%). This compound, which is evidently 1-*benzoylanthrapurpurin* 2 : 7-*dimethyl ether*, by hydrolysis with methyl-alcoholic potash, yielded orange-yellow needles of anthrapurpurin 2 : 7-dimethyl ether, m. p. 242—243°, a substance which has been previously prepared by Graebe and Bernhard (*Annalen*, 1906, **349**, 222) (Found: C, 67·45; H, 4·4%). The barium salt of the 1 : 7-dimethyl ether is soluble in water, whereas that of the 2 : 7-dimethyl ether is insoluble. Acetylation gave 1-acetylanthrapurpurin 2 : 7-dimethyl ether as pale yellow needles, m. p. 228—230°.

Purpurin.—Commercial purpurin was extracted with boiling (purified) solvent naphtha. The crystals which separated from the extract on cooling were employed without further purification.

2-*Acetylpurpurin*. To a well-stirred mixture of potassium acetate (1 g.) and cold acetic anhydride (10 c.c.) purpurin (2 g.) was added. After being kept over-night, the product was collected and recrystallised from alcohol, forming orange needles, m. p. 179—

180°. Alternatively, purpurin (10 g.) in pyridine (100 c.c.) was treated gradually with acetic anhydride (4 c.c.) and after 1 hour water was slowly added. The deposit was recrystallised from alcohol (Found: C, 64·2; H, 3·5. $C_{16}H_{10}O_6$ requires C, 64·4; H, 3·35%). Hydrolysis gave 85·5% of purpurin (Calc., 85·9%).

Methylation. 2-Acetylpurpurin (2 g.) in tetrachloroethane (30 c.c.) (ether and acetone also were employed as solvents) was treated with diazomethane from nitrosomethylurethane (10 c.c.). After 2 days, the solution was steam-distilled, the viscid product dried as completely as possible and extracted with ether (insoluble residue A), the extract evaporated, and the residue crystallised from alcohol (yield, 0·15 g.) (Found: C, 66·35; H, 4·5; CH_3, 9·0. $C_{18}H_{14}O_6$ requires C, 66·1; H, 4·3; CH_3, 9·2%).

1-Acetylpurpurin 2 : 4-dimethyl ether forms lemon-yellow needles, m. p. 189—190°, and when hydrolysed with hydrochloric acid in the usual manner, gives fine, orange needles of *purpurin 2 : 4-dimethyl ether*, m. p. 186—189° (Found: C, 67·55; H, 4·0. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%).

The residue (A) undissolved by the ether was extracted with boiling acetone, and the crystals deposited from the extract were recrystallised from acetone. 1-*Acetylpurpurin* 2-*methyl ether* was thus obtained as yellow needles, m. p. 224—225° (Found: C, 65·5; H, 3·8. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·8%). Acetylation employing pyridine gave yellow needles of 1 : 4-*diacetylpurpurin 2-methyl ether*, m. p. 170—172°, and by hydrolysis with hydrochloric acid, fine, brick-red needles of purpurin 2-monomethyl ether, m. p. 232—233°, soluble in alkalis with a crimson coloration, were obtained (Found: C, 66·6; H, 3·6; CH_3, 5·5. Calc. for $C_{15}H_{10}O_5$: C, 66·7; H, 3·7; CH_3, 5·5%). It is identical with the methyl ether, described as melting at 228—230°, obtained by Perkin (*loc. cit.*) from monopotassium purpurin and methyl iodide.

Purpuroxanthin.—For the preparation of this compound, purified purpurin (*loc. cit.*) was reduced with sodium hydrosulphite. Before crystallisation the elimination of sulphur with carbon disulphide was necessary.

3-Acetylpurpuroxanthin was prepared from potassium acetate (2·5 g.), acetic anhydride (15 c.c.), and purpuroxanthin (5 g.) in the cold (see purpurin). The product crystallised from alcohol (charcoal) as long, yellow needles, m. p. 144° (Found: C, 68·0; H, 3·6. $C_{16}H_{10}O_5$ requires C, 68·1; H, 3·5%).

Methylation. 3-Acetylpurpuroxanthin (2 g.), tetrachloroethane (40 c.c.), and nitrosomethylurethane (8 c.c.) were employed. After 3 days, the product was distilled with steam and the well-dried tarry residue dissolved in boiling alcohol (60 c.c.) (charcoal). An

amorphous precipitate separated (Filtrate A) which by crystallisation from the same solvent formed lemon-yellow leaflets (0·78 g.) of 3-*acetylpurpuroxanthin* 1-*methyl ether*, m. p. 154—155° (Found: C, 68·8; H, 4·2; CH_3, 5·3. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·0; CH_3, 5·0%). Hydrolysis with hydrochloric acid gave *purpuroxanthin* 1-*methyl ether*, which separated from acetone as yellow leaflets, m. p. 311—313° (Found: C, 71·1; H, 4·1. $C_{15}H_{10}O_4$ requires C, 70·8; H, 3·9%). The high melting point of this compound, compared with that of the 3-methyl ether, which melts at 193° (Graebe and Bernhard, *loc. cit.*), suggested that this compound was in reality a methylpurpuroxanthin methyl ether, formed by the entry of a methyl group into the ring during methylation. This, however, was not the case, as demethylation with fuming hydrochloric acid at 180° yielded purpuroxanthin, identified as diacetylpurpuroxanthin, m. p. 178—181°. The presence of a second acetylpurpuroxanthin methyl ether in filtrate (A) could not be detected.

Alizarin.—2-*Benzoylalizarin.* (*a*) 2-Acetylalizarin (3 g.) in chloroform (15 c.c.) and benzoyl chloride (3 g.) was slowly treated with pyridine (3 c.c.). Crystals of 2-*benzoyl*-1-*acetylalizarin* gradually separated, and the amount was increased by the addition of alcohol to the mixture (yield, 3 g.). Recrystallisation from acetone gave yellow needles, m. p. 172—174° (Found: C, 71·4; H, 3·6. $C_{23}H_{14}O_6$ requires C, 71·5; H, 3·6%). Hydrolysis was effected by employing hydrochloric acid (5 c.c.) in acetic acid (30 c.c.) at 100° for 3 hours, the 2-benzoylalizarin thus obtained separating from its solution in pyridine as long, orange-yellow needles, m. p. 220—221° (Found: C, 73·1; H, 3·6. $C_{21}H_{12}O_5$ requires C, 73·2; H, 3·5%).

(*b*) 2-Potassioalizarin (from 2-acetylalizarin and alcoholic potassium acetate), suspended in chloroform, was treated with benzoyl chloride. After keeping, the orange-yellow crystals were collected, washed with dilute ammonia to remove traces of alizarin, and recrystallised from pyridine. The product melted at 220—221° and was identical with the benzoylalizarin obtained by method (*a*), which is consequently the 2-benzoyl compound. Acetylation gave the 2-benzoyl-1-acetylalizarin described above, indicating that migration of the benzoyl group does not occur when the latter compound is hydrolysed.

Methylation. 2-Benzoylalizarin (2 g.), tetrachloroethane (30 c.c.), and nitrosomethylurethane (8 c.c.) were employed, and after 2 days the crystalline deposit (0·35 g.) was collected (Filtrate A) and recrystallised from much benzene. 1-*Benzoylalizarin* 2-*methyl ether* thus separated as a pale yellow, crystalline powder, m. p. 266—

268° (Found: C, 73·7; H, 3·8. $C_{22}H_{14}O_5$ requires C, 73·4; H, 3·95%). Hydrolysis with 1% alcoholic potash gave a red solution which on dilution with water and acidification deposited orange-red needles of alizarin 2-methyl ether, m. p. 228—230°, from which the acetyl derivative, m. p. 204—206°, was prepared. 1-Benzoylalizarin 2-methyl ether can be readily prepared from alizarin 2-methyl ether (1 g.), chloroform (60 c.c.), and benzoyl chloride (1 c.c.), pyridine (1 c.c.) being gradually added. The pale orange crystals were collected and washed with alcohol (1·25 g.). They had the properties described above.

The mother-liquor (A) was steamed-distilled and the residue fractionally crystallised from benzene to remove a trace of 1-benzoylalizarin 2-methyl ether. The main and more soluble fraction, consisting of 2-benzoylalizarin 1-methyl ether (0·8 g.), was isolated as yellow prisms, m. p. 203—205° (Found: C, 73·4; H, 4·0. $C_{22}H_{14}O_5$ requires C, 73·4; H, 3·95%). Hydrolysis with 1% methyl-alcoholic potash (as with the previously described compound) gave hair-like needles of alizarin 1-methyl ether, m. p. 175—177° (Found: C, 70·7; H, 4·1%), the acetyl derivative of which melted at 211—212°. The main product of the methylation of 2-benzoylalizarin is thus 2-benzoylalizarin 1-methyl ether.

Diethylcarbonatoalizarin was prepared from alizarin (1 g.), chloroform (6 c.c.), ethyl chloroformate (2 g.), and pyridine (2 c.c.), the mixture being kept for 2 days. The product (1 g.), recrystallised from alcohol, formed yellow needles, m. p. 150—157° (Found: C, 62·5; H, 4·3. $C_{20}H_{16}O_8$ requires C, 62·5; H, 4·2%).

2-Ethylcarbonatoalizarin. Commercial alizarin (5 g.) in pyridine (50 c.c.) was treated with ethyl chloroformate (2·1 g.) and after 30 minutes water was slowly added, the mixture being well shaken. The product (4·6 g.), recrystallised first from alcohol and then from acetone, consisted of flat, yellow needles, m. p. 138—140° (Found: C, 65·5; H, 4·0. $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·85%).

Methylation. 2-Ethylcarbonatoalizarin (2 g.) in ether (50 c.c.) was treated with diazomethane from nitrosomethylurethane (8 c.c.), and the mixture kept for 2 days. The long, yellow needles (1·2 g.) were collected (A) and the filtrate was evaporated to dryness. By trituration with alcohol the viscid residue gave crystals (0·4 g.) (B). From (A) by recrystallisation from small amounts of benzene, almost colourless plates or prisms, m. p. 213—215°, were obtained (Found: C, 66·7; H, 4·4. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%). This compound, 1-*ethylcarbonatoalizarin* 2-*methyl ether*, by hydrolysis with alcoholic potash gave alizarin 2-methyl ether.

The benzene filtrates (A) were evaporated to dryness, the residue was added to (B), and the mixture fractionally crystallised from

lcohol. The main and more soluble fraction formed yellow needles, a. p. 145—147° (Found: C, 66·1; H, 4·45%), evidently 2-*ethyl-arbonatoalizarin* 1-*methyl ether*, from which, by hydrolysis in the isual manner, hair-like needles of alizarin 1-methyl ether were btained (Found: C, 68·8; H, 4·2%).

To determine whether the migration of the acyl group (in this ase the ethylcarbonato-group) is influenced by the amount of liazomethane used in the methylation process, the foregoing xperiment (I) was repeated, and a second (II), employing 12 c.c. of itrosomethylurethane, simultaneously carried out, the conditions eing identical in each case. The crystalline deposit (compare A above) from Experiment I gave by fractional crystallisation from enzene 0·44 g. of 1-ethylcarbonatoalizarin 2-methyl ether, and he residue obtained by the evaporation of the combined mother-iquors yielded on hydrolysis 1·1 g. of crude alizarin 1-methyl ether, quivalent to 1·41 g. of 2-ethylcarbonatoalizarin 1-methyl ether. In Experiment II, 1-ethylcarbonatoalizarin 2-methyl ether (0·45 g.) and crude alizarin methyl ether (1·11 g.) equivalent to 2-ethyl-carbonatoalizarin 1-methyl ether (1·42 g.) were obtained. As by acetylation the crude alizarin 1-methyl ether from (I) gave 0·88 g., and that from (II) 0·86 g., of pure acetyl compound, m. p. 211—213°, it appears evident that the migration of the acyl group is not materially affected by an increase in the concentration of the diazomethane present.

*2-Toluene-*p*-sulphonylalizarin.* To a well-cooled mixture of alizarin (0·5 g.) and toluene-*p*-sulphonyl chloride (0·8 g.) in chloroform (3 c.c.) pyridine (0·8 c.c.) was gradually added. After 1 hour, dilution with alcohol caused the separation of orange-yellow plates, which were recrystallised from alcohol and acetic acid; they then melted at 218—219° (Found: C, 64·0; H, 3·6; S, 8·2. $C_{21}H_{14}O_6S$ requires C, 64·0; H, 3·55; S, 8·1%).

Methylation. A solution of 2-toluene-*p*-sulphonylalizarin (2 g.) in warm tetrachloroethane, cautiously cooled to avoid the separation of crystals, was at once treated with diazomethane (nitrosomethylurethane, 8 c.c.) and kept for 2 days. Steam distillation gave a crystalline residue which after recrystallisation from acetic acid–methyl alcohol melted at 176—177° (yield, 1·5 g.) (Found: C, 64·5; H, 4·1. $C_{22}H_{16}O_6S$ requires C, 64·7; H, 3·9%). The hydrolysis of this compound with boiling 2% methyl-alcoholic potash could only be gradually effected, the claret-red liquid being decanted from time to time, and the unattacked residue treated with fresh amounts of reagent until all had passed into solution. For 0·5 g. of substance 200 c.c. of the alcoholic potash were employed. The alkaline solution, diluted with water, acidified,

and boiled to expel alcohol, gave needles of alizarin 1-methyl ether m. p. 181—182° (Found: C, 70·8; H, 4·1%). The alcoholic-acetic acid mother-liquors when evaporated to dryness gave a residue from which, by hydrolysis, only alizarin 1-methyl ether was obtained. It is thus evident that in these circumstances a migration of the toluene-*p*-sulphonyl group does not occur.

Anthragallol.—2 : 3-*Diethylcarbonatoanthragallol.* To anthragallol (2 g.) in pyridine (20 c.c.), ethyl chloroformate (2·6 c.c.) was gradually added and the mixture kept for 30 minutes. On addition of water (20 c.c.) and thorough shaking, crystals (1·9 g.) separated, which were recrystallised first from benzene (charcoal) and then from acetone. The orange-coloured prisms melted at 174—175° (Found: C, 60·9; H, 4·1. $C_{20}H_{16}O_9$ requires C, 60·0; H, 4·0%).

Methylation. 2 : 3-Diethylcarbonatoanthragallol (4 g.) was treated with diazomethane as described under diethylcarbonatoanthrapurpurin, and the product steam-distilled. A solution of the residue in boiling alcohol containing acetone gave crystals which by recrystallisation from acetone were obtained as large yellow prisms, m. p. 125—127°. The yield of this compound, possibly 2 : 3- or 1 : 2-*diethylcarbonatoanthragallol* 1-(or 3)*methyl ether*, was 3·13 g. (Found: C, 60·7; H, 4·1. $C_{21}H_{18}O_9$ requires C, 60·9; H, 4·3%). From the acetone mother-liquors a product was isolated which after fractional crystallisation from alcohol formed pale yellow needles (0·12 g.), m. p. 196—197°, which apparently consisted of 1 : 3-*diethylcarbonatoanthragallol* 2-*methyl ether* (Found C, 60·9; H, 4·6%). These products will be further examined.

Gallacetophenone.—The commercial product Alizarine Yellow C was recrystallised from water (charcoal) until of constant melting point.

Diacetylgallacetophenone. Gallacetophenone (5 g.) in cold acetic acid (15 c.c.) and acetic anhydride (7 c.c.) was treated with pyridine (2 c.c.), drop by drop, and kept for 18 hours. The solution was then poured into water (400 c.c.), and the precipitate collected dried on tile, and crystallised from alcohol. The long, colourless needles melted at 107—108° (Found: C, 57·2; H, 4·9; Ac, 34·15 $C_{12}H_{12}O_6$ requires C, 57·1; H, 4·8; Ac, 34·1%).

Methylation. Diacetylgallacetophenone (2 g.), tetrachloroethane (10 c.c.), and nitrosomethylurethane (8 c.c.) were employed. After 3 days, colourless plates (A) (0·96 g.) had separated which after recrystallisation from alcohol melted at 150—151° (Found: C 58·7; H, 5·3; CH_3, 5·7. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3; CH_3 5·5%). This compound, 2 : 4-*diacetylgallacetophenone* 3-*methyl ether* treated with boiling aqueous sodium carbonate, gave eventually a clear solution, from which, when neutralised, long needles of wa-

gallacetophenone 3-methyl ether, m. p. 134—135°, separated (Found: C, 59·7; H, 5·4. Calc. for $C_9H_{10}O_4$: C, 59·3; H, 5·5%). As re-acetylation gave the acetyl compound melting at 150—151°, a migration of the methyl group does not occur during the subsequent hydrolysis of this compound. This substance, as already indicated, is identical with that, m. p. 132—133°, obtained from 2-potassio-gallacetophenone by Perkin and Allen (*loc. cit.*), who gave the melting point of the acetyl derivative as 146—148°.

The tetrachloroethane filtrate from (A) was steam-distilled and the residual aqueous liquid, which deposited needles, m. p. 143—147°, was treated with boiling aqueous sodium carbonate to hydrolyse the acetyl compound present. The neutralised solution was evaporated to dryness, the residue extracted with boiling alcohol, and the solution clarified with charcoal and treated in the cold with alcoholic lead acetate. The lead salt of gallacetophenone 3-methyl ether thus precipitated (from which a further quantity of this 3-methyl ether was isolated) was removed, and the filtrate rendered faintly acid with sulphuric acid and evaporated to dryness. A concentrated methyl-alcoholic extract of the residue slowly deposited prisms of *gallacetophenone* 2- or 4-*methyl ether*, which after recrystallisation melted at 175° (Found: C, 59·1; H, 5·6%). Whereas gallacetophenone 2- or 4-methyl ether gives with alcoholic lead acetate a lead salt soluble in alcohol but insoluble in water, the lead compound of the 3-methyl ether is insoluble in alcohol and soluble in water.

Ditoluene-p-*sulphonylgallacetophenone*. A well-cooled mixture of gallacetophenone (1 g.), chloroform (6 c.c.), and toluene-*p*-sulphonyl chloride (4·6 g.) was slowly treated with pyridine (1·6 c.c.). After 1 hour, the product, diluted with alcohol (15 c.c.), was treated cautiously with water. The colourless plates (2·14 g.), thus obtained, recrystallised from methyl alcohol, melted at 152—153° (Found: C, 55·3; H, 4·3; S, 13·5. $C_{22}H_{20}O_8S_2$ requires C, 55·5; H, 4·2; S, 13·4%).

Methylation. This compound (2 g.), tetrachloroethane (15 c.c.), and nitrosomethylurethane (15 c.c.) were employed, the mixture being kept for 2 days. Distillation with steam yielded a pale yellow, oily residue, which was dried and dissolved in methyl alcohol (10—15 c.c.) (charcoal). On keeping, clusters of colourless needles (1·3 g.) of *ditoluene*-p-*sulphonylgallacetophenone* 2- or 4-*methyl ether*, m. p. 111—113°, separated (Filtrate A) (Found: C, 56·3; H, 4·6; CH_3, 3·1. $C_{23}H_{22}O_8S_2$ requires C, 56·3; H, 4·5; CH_3, 3·1%). Digestion with boiling 2% methyl-alcoholic potash, dilution with water, and neutralisation gave crystals of *gallacetophenone* 2- or 4-*methyl ether*, which, after recrystallisation from methyl alcohol, melted at 175° (Found: C, 59·2; H, 5·3%).

The methyl-alcoholic mother-liquor (A) was boiled with a littl alcoholic potash for a short time to hydrolyse any ditoluene-p sulphonyl compound present, and the solution acidified. Examin ation of the viscid mass revealed the absence of gallacetophenon 3-methyl ether and it was thus apparent that only ditoluene-p sulphonylgallacetophenone 2- or 4-methyl ether is produce when ditoluene-*p*-sulphonylgallacetophenone is methylated wit diazomethane.

Position of the Methoxy-group in the Gallacetophenone Methyl Ether —Gallacetophenone methyl ether (1 g.) melting at 150—151° wa heated with alcoholic potash for 4 hours at 180° in a sealed tube The solution, diluted with water and freed from alcohol by evapor ation, was saturated with carbon dioxide and repeatedly extracte with ether to remove unattacked substance. From the acidifie liquid, ether removed a viscid product, containing evidently methyl ether of pyrogallolcarboxylic acid, and this was furthe purified by extraction with sodium bicarbonate in order to remov the last traces of gallacetophenone methyl ether. The product b dry distillation yielded a yellow oil, which gave a violet coloratio with ferric chloride solution, an indication of the presence of pyr gallol 2-methyl ether. The acetyl compound crystallised fro ligroin in colourless needles, m. p. 60—63°, and although accordin to Herzig and Pollak (*Monatsh.*, 1904, **25**, 808) 1 : 3-diacety pyrogallol 2-methyl ether melts at 51—54°, there can be no dout as to its identity with the compound produced as above state from gallacetophenone 3-methyl ether. A similar experiment wit the gallacetophenone methyl ether melting at 175° gave as fin product a colourless oil, the acetyl compound of which melted a 87—89° (diacetylpyrogallol 1-methyl ether melts at 91—93° *Monatsh.*, 1904, **25**, 501). As this crude methyl ether yielded a olive coloration with ferric chloride solution, it evidently containe pyrogallol 1-methyl ether, and this must have originated fro either the 2- or the 4-methyl ether of gallacetophenone.

We are much indebted to the British Alizarine Co., Ltd. for gift of commercial alizarin, purpurin, and anthrapurpurin.

CLOTHWORKERS' RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS. [*Received, November 30th*, 1927.]

XXXV.—*Orientation Effects in the Diphenyl Series. Part V. The Independence of the Two Nuclei in Diphenyl Compounds.*

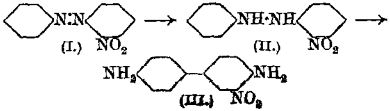
By RAYMOND JAMES WOOD LE FÈVRE and EUSTACE EBENEZER TURNER.

The Nitration of Phthalylbenzidine and the Preparation of 3-Nitrobenzidine.

ON a previous occasion (J., 1926, 2041) we stated that 2-nitrobenzidine, m. p. 143°, is obtained on hydrolysing the product of nitrating phthalylbenzidine in excess of concentrated sulphuric acid. Koller, on the other hand, isolated as the sole product a red, crystalline solid, m. p. 192°, which he regarded as 3-nitrobenzidine (*Ber.*, 1904, **37**, 2880). In view of Koller's very definite statements, we have re-investigated the above nitration and also prepared 3-nitrobenzidine by a process which established its constitution. Precise repetition of Koller's nitration has led to excellent yields of 2-nitrobenzidine, together with a small quantity of a mixture of substances melting at 185—195° which is not separable into its components, and corresponds in these and other respects to a mixture of 2-nitro- and 2 : 3′-dinitro-benzidine.

The preparation of 3-nitrobenzidine has presented many difficulties. We first attempted to obtain it by nitrating a number of *NN′*-disubstituted benzidines. The mononitration of diacetylbenzidine has already been shown (*loc. cit.*) to be impracticable owing to the insolubility of this substance in any nitrating mixture which does not effect dinitration. We now find that benzidine condenses rapidly with most esters at the boiling point of the latter, and in this way 4 : 4′-*diethyloxamidodiphenyl*, $(CO_2Et{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot})_2$, and similar compounds have been prepared. This compound and *NN′*-dicarbethoxybenzidine, $(CO_2Et{\cdot}NH{\cdot}C_6H_4{\cdot})_2$, are considerably more soluble than diacetylbenzidine, yet neither compound could be caused to undergo mononitration only. Dinitration is readily effected, and that of the oxamido-derivative affords what is up to the present the most convenient method of preparing Strakosch's dinitrobenzidine.

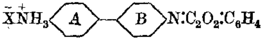
A second synthesis of 3-nitrobenzidine was attempted by the process (I) ⟶ (II) ⟶ (III) :



Bamberger and Hübner (*Ber.*, 1903, **36**, 3803) found that 2-nitroazobenzene was converted by alkali sulphides into 2-phenylbenztriazole 1-oxide, but Green and Bearder (J., 1911, **99**, 1960) effected the reduction of 2 : 2′-dinitroazobenzene to the corresponding hydrazo-compound. On submitting 2-nitroazobenzene to Green and Bearder's reduction conditions, however, we obtained the triazole oxide as the sole product.

The preparation of 3-nitrobenzidine was finally accomplished by reducing 3 : 4′-dinitro-4-aminodiphenyl (IV) with hot aqueous-alcoholic ammonium sulphide, this method being suggested by the known stability of *o*-nitroaniline towards this reagent. 3-*Nitrobenzidine* is almost insoluble in alcohol, from which solvent Kolle

(IV.)

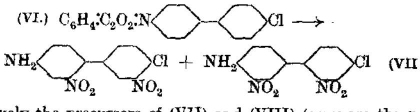


(V.)

claimed to have crystallised it. It melts at least 15° higher tha Koller's product. Its diacetyl derivative, clearly the first stag in the formation of Strakosch's dinitrobenzidine from diacety benzidine, affords 3 : 3′-dinitrodiacetylbenzidine on nitratio Moreover, 3-nitrobenzidine depresses the m. p. of the produc m. p. 185—195°, obtained by us from phthalylbenzidine, so that it probable that little if any 3-nitrobenzidine is formed in the latt process. The absence of appreciable amounts of the 3-nitro-con pound suggests that nitration occurs in nucleus B (V) rather th in (A).

Mononitration of 4-*chloro-4′-phthalimidodiphenyl* (VI) could not effected, and dinitration, followed by hydrolysis, gave a mixture (VII) and (VIII). It is probable that 4-chloro-2′-nitro-4′-phth imidodiphenyl and 4-chloro-2-nitro-4′-phthalimidodiphenyl

(VI.)



(VII.) (VII

respectively the precursors of (VII) and (VIII) (compare the r ation of 4 : 4′-dihalogenodiphenyls; Dennett and Turner, J., 1 476). 4-*Bromo-4′-phthalimidodiphenyl* also has been found undergo 2 : 3′- and 2′ : 3-nitration.

The Independence of the Two Nuclei.

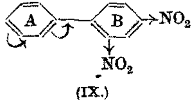
Superficial consideration of the known orienting effects in diphenyl series suggests that a group present in one nucleus (a in IX) has a direct influence on the position or positions taken u

a second group entering the other nucleus (A). We do not, however, think this is the case, and prefer to regard the first substituent as producing its effect indirectly, that is, merely by modifying the orienting properties of nucleus B. The modified B nucleus remains ortho-para directing whatever the nature of the first substituent, and a group then entering nucleus A invariably takes up the 4'- (to a lesser extent the 2'-) position. When the 4'-position is occupied by an ortho-para directing group, the modified B nucleus frequently appears to exert quite a small ortho-para influence.

Were a direct orienting effect transmitted from a group present in nucleus B to substitutable positions in A, 2- and 4-nitrodiphenyl would be expected to undergo at any rate a certain amount of 3'-nitration, since the source of electron drift will be the 4'-carbon atom (IX). Since 3'-nitration does not occur, it is clear that in this sense A and B are independent. Similarly, from the work of Burton and Kenner (J., 1922, **121**, 489) and from some experiments we have made, it seems probable that nitro-groups present in one nucleus cannot effect the activation of halogen atoms or nitro-groups present in the other nucleus.* Both sets of facts agree with the conception of A and B as two independent mobile *cyclo*hexatrienoid *systems connected in the 1 : 1'-positions by an invariable single bond, which is not a link in a true conjugated system.*

The nitration of 2- or 4-nitrodiphenyl may be compared with that of ω-nitrostyrene. Here there is no mobile conjugation (electronic tautomerism) between the side chain and the nucleus, and therefore the effect of the nitro-group cannot be transmitted to the nucleus to any extent. Again, therefore, meta-nitration does not occur.

The assumption of mobility of conjugation throughout the naphthalene molecule appears to explain the nitration of α-nitronaphthalene in positions 5, 8, and 3 (compare Pictet, *Compt. rend.*, 1893, **116**, 815) (formulæ X and XI). There are doubtless factors



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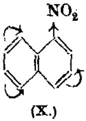
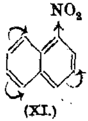


(X.)



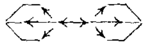
(XI.)

other than a simple electron drift regulating substitution in naphthalene compounds, but we think it worth while to point out the

* After this paper had been written, the authors noticed that Robinson and Zaki (J., 1927, 2485) had arrived at very similar conclusions from a different point of view.

contrast between naphthalene and diphenyl. It is likely that a halogen atom or a nitro-group present in position 5 or 7 in naphthalene would be rendered reactive if nitro-groups were present in positions 1 and 3.

The discussion of the independence of the two benzene nuclei in diphenyl derivatives leads us to a recent paper by Bell and Kenyon (J., 1926, 3044). These authors criticise adversely a formula (XII) suggested by one of us (*Nature*, 1923, **112**, 439) at a time when, *as we now know, the very facts of diphenyl chemistry were untrust*worthy. It is clear that recent work in the diphenyl series does not necessitate formula (XII), except in such a modernised form as (XIII), which, however, is by no means unsatisfactory as a basi

(XII.)  (XIII.)

for explaining the laws of substitution in the diphenyl series. W must, however, differ with Bell and Kenyon in the interpretatio of their experimental results. They found that 4-hydroxydiphen coupled with benzenediazonium chloride in position 3, and react with chloroform in the presence of alkali to give what they regarde we think rightly, as the 3-aldehyde. They stated that formu (XII) "*demands*" 4′-reaction in both cases. Yet few will disse from the view that the orienting effect of the charged oxygen at decreases with distance, and it is curious that Bell and Keny should have overlooked the fact that on the basis of formula (X the 4′-position is not less than three times as distant as the 3- a 5-positions, which (compare the 3- and 5-positions in *p*-cresol) in any case *competing for the reagent*. Nor is it certain that the t reactions chosen do not depend on the possibility of keto-e tautomerism, which would be clearly impossible between the and 4′-positions in 4-hydroxydiphenyl, but probable between 3- and 4-positions.

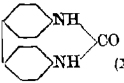
Had these authors used a 3 : 5-disubstituted hydroxydiphe their results might have borne their interpretation. We find 3 : 5-dibromo-4-hydroxydiphenyl, a substance prepared by Bell Kenyon (*loc. cit.*), does not couple at any measurable rate diazotised sulphanilic acid, a reagent used because of its kn advantages as compared with diazotised aniline.

We have not investigated the Reimer–Tiemann reaction wit dibromo-compound, because so little is known of the mechanis this reaction, which is neither unidirectional nor quantitative. experiment, however, settles the point raised, *i.e.*, it shows tha charged oxygen atom present (in alkaline solution) in 4-hyd [illegible] confer reactivity on the 4′-position.

The Condensation of Benzidine with Carbamide.

Schiff and Vanni (*Annalen*, 1890, **258**, 363), by heating "benzid-
ıediurethane" with benzidine, obtained a substance which they
egarded as (XIV) identical with a compound previously obtained
y Schiff (*Ber.*, 1878, **11**, 830) by heating henzidine with carbamide.
n neither of these papers, however, were any analyses quoted.
Iichler and Zimmermann, apparently unaware of the results of
Schiff (1878, *loc. cit.*), prepared "carbonylbenzidine" by the
nteraction of carbonyl chloride and benzidine, and considered this
ompound also to have formula (XIV) (*Ber.*, 1881, **14**, 2178).

Snape (*Chem. News*, 1896, **73**, 37), by treating diphenyl-4 : 4'-
licarbimide, $NCO\cdot C_6H_4\cdot C_6H_4\cdot NCO$, with ammonia, obtained a com-
ound which was in turn stated, on very slight evidence, to be
dentical with Schiff's compound. From its mode of formation, it
s almost certainly (XV).


(XIV.)

(XV.)

The present authors have shown (J., 1926, 2476) that the "carb-
onylbenzidine" of Michler and Zimmermann is certainly not
XIV) but is either $(NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH)_2CO$ or a substance of more
omplex structure, *e.g.*, as produced by the reaction :

$$EtO_2C\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot CO_2Et + 2NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2 = 2EtOH + (NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot)_2.$$

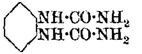
We have prepared Schiff's benzidine-carbamide compound and
egard it as identical with Snape's compound and not with the
ınknown carbonylbenzidine (XIV) nor with the "carbonyl-
benzidine" of Michler and Zimmermann, for on subliming, the
atter compound does not decompose, whereas the condensation
product of benzidine and carbamide does. Moreover, one molecule
of benzidine always reacts with two molecules of carbamide when
he two substances are heated together in various proportions.
Conclusive evidence cannot be obtained owing to the chemical and
physical properties of the substances concerned.

In view of the present position of the Kaufler formula, analogies
will no longer be expected between pairs of substances such as
benzidine and *o*-phenylenediamine. These two bases behave quite
lifferently towards carbamide. The former, according to the
evidence given above, reacts with carbamide as does aniline, with
he formation of the analogue of phenylcarbamide, $NH_2\cdot CO\cdot NHPh$,
whereas the latter is converted into 2-hydroxybenziminazole (XVI)
(Kym, *J. pr. Chem.*, 1907, **75**, 323), the analogue of the hypothetical

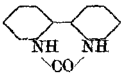
carbonylbenzidine (XIV). Moreover, as Hartmann showed (*Ber.* 1890, **23**, 1047), *o*-phenylenediamine hydrochloride is converted b carbonyl chloride into the above benziminazole, but by potassiun cyanate into an entirely different substance, "*o*-phenylene di ureide" (XVII) (Lellmann, *Ber.*, 1883, **16**, 598). A close analog has been repeatedly observed between 1 : 2-disubstituted benzen derivatives and 2 : 2′-disubstituted diphenyl compounds. In th present case, the analogy holds, for 2 : 2′-diaminodiphenyl i converted by carbamide into a true carbonyldiaminodipheny (XVIII) (Niementowski, *Ber.*, 1901, **34**, 3325).

The condensation product of benzidine and carbamide, *i.e.* *NN′*-dicarbamylbenzidine, dissolves in concentrated sulphuric aci to give a solution which is coloured an intense reddish-purple b traces of nitrates. One gram of potassium nitrate could thus b detected in 500,000 c.c. of concentrated sulphuric acid. At greate dilutions, the test failed; diphenylamine, however, still gave a coloration after the addition of water. The new reagent is un affected by nitrites when present at about the same concentration as the nitrates.

(XVI.)



(XVII.)



(XVIII.)

EXPERIMENTAL.

Nitration of Phthalylbenzidine.—Phthalylbenzidine (50 g.) pre viously crystallised from nitrobenzene (compare Kuhn, Jacob, and Furter, *Annalen*, 1927, **455**, 254) was nitrated in sulphuric acid at $-10°$ according to the directions of Koller (*loc. cit.*). After $\frac{1}{2}$ hour the solution was poured on ice, and the brown, gelatinous pre cipitate obtained was filtered off and washed by suspension in ho water, steaming, and filtration while hot. The cooled yellov filtrate, on being basified with ammonia, gave a bright red substanc (A) (1·2 g.), m. p. 156—160°.

A solution of the residual paste in 250—300 c.c. of concentrated sulphuric acid was heated at 130° for 30 minutes, cooled, and diluted with much water, 7 g. of a dark reddish powder (B) being obtained. The filtrate, when partly basified, gave a light yellow powder (C) (20 g.), m. p. above 225°. The filtrate from this, on complete basification, gave a red, gummy solid which, after being steamed, changed to a red, crystalline suspension (D) (11 g.) m. p. 140—141°. The m. p. of this product was not lowered by admixture with 2-nitrobenzidine.

Fraction A was extracted with alcohol, leaving a sparingly soluble yellow powder. The extract deposited an indefinite red powder, m. p. about 175°. Further crystallisation did not affect the m. p. of this product, which was, however, clearly a mixture. The mother-liquors from these crystallisations were precipitated with water, giving a bright red powder (0·5 g.), m. p. 191—195° with previous shrinking. A mixture of this product with 3-nitrobenzidine melted indefinitely at 185—190°.

B and C contained unhydrolysed phthalyl compounds. Hydrolysis was effected with alcoholic-aqueous potassium hydroxide at a temperature not exceeding 40°, and the solution was somewhat diluted and filtered (Filtrate E). The residue (dark red, 11 g.) was freed from inorganic matter (5·7 g.) by extraction with boiling alcohol. Evaporation of the extract gave 4 g. of red crystals, m. p. 128—130°. These were combined with 5 g. of similarly melting material obtained by the complete dilution of E and the whole was crystallised from hot 70% sulphuric acid. A cream-coloured paste of the 4 : 4'-disulphate was obtained, and this changed into the yellow 4-sulphate on addition of water. Complete neutralisation of the yellow sulphate gave 5·5 g. of a deep red solid, m. p. 134—137°. Mixed with 2-nitrobenzidine, this melted at 136—137°. Extraction with much alcohol left a residue (0·7 g.), m. p. 190—200°, which, after being crystallised from phenol–alcohol, had m. p. 210—215°.

The total yield of 2-nitrobenzidine is estimated as 20 g. (theoretical yield, for mononitration, 27 g.; but some dinitration clearly occurred).

Condensation of Esters with Benzidine.—The following substances of high m. p. were obtained by gently boiling a solution of benzidine in excess of the appropriate ester under reflux for the times stated, and were isolated by addition of alcohol, filtration, and extraction with boiling alcohol.

NN'-*Di-o-carbethoxybenzoylbenzidine.*—After ½ hour, the ethyl phthalate solution deposited small, yellow plates. These melted above 300° and were insoluble in all common solvents (Found: N, 5·6. $C_{32}H_{28}O_6N_2$ requires N, 5·3%).

4 : 4'-*Diethyloxamidodiphenyl.*—After ½ hour (ethyl oxalate being used), a sudden deposition of pearly plates occurred. These were very slightly soluble in hot glacial acetic acid and crystallised from this solvent in plates (Found: N, 7·5. $C_{20}H_{20}O_6N_2$ requires N, 7·3%).

NN'-*Dicinnamoylbenzidine.*—After 30 minutes (ethyl cinnamate being used), yellow crystals appeared, but heating was continued for another hour. The final product was a yellow, crystalline powder,

insoluble in ordinary solvents (Found : N, 6·7. $C_{30}H_{24}O_2N_2$ requir N, 6·3%).

NN'-*Dicarbethoxybenzidine*.—The following method was foun preferable to that given by Schiff and Vanni (*loc. cit.*). Wel powdered benzidine (30 g.) was treated slowly with 30 g. (almo 2 mols.) of ethyl chloroformate, the flask being warmed gentl during the process, and kept well shaken. The pasty mass graduall became a loose powder. About 20 c.c. of alcohol were added, fo lowed later by warm dilute hydrochloric acid. The liquid wa filtered, and the extraction with acid repeated until the filtrate n longer set to a stiff gel on cooling. The residue was crystallise from 270 c.c. of boiling glacial acetic acid. Dilution of the acet acid mother-liquor also gave stiff gels.

3 : 3'-*Dinitrobenzidine*.—4 : 4'-Diethyloxamidodiphenyl (5 g.) wa slowly dissolved in a mixture of 35 c.c. of nitric acid (*d* 1·5) and 25 c. of glacial acetic acid, the temperature being kept below 25°. Aft 5 minutes, the reddish solution was gradually diluted; needle separated, and these crystallised from 200 c.c. of glacial acetic aci in yellow needles, m. p. 216—217° (Found : N, 11·7. $C_{20}H_{18}O_{10}N$ requires N, 11·8%). Hydrolysis with 60—70% sulphuric aci gave a crude base, m. p. 273—274°.

Attempts to effect mononitration of the oxamido-derivativ led either to unchanged material or to impure dinitro-com pound.

Dinitration of NN'-*Dicarbethoxybenzidine*.—This compound (2 g.) dissolved in 50 c.c. of glacial acetic acid, was treated with 1·5 g. o nitric acid (*d* 1·5) dissolved in 5 c.c. of glacial acetic acid. Afte 1 hour's heating at 90—100°, separation of yellow crystals (2 g. was complete. The 3 : 3'-dinitro-compound so obtained crystallise from rectified spirit in plates, m. p. 216—217° (Found : N, 13·6 $C_{18}H_{20}O_8N_4$ requires N, 13·3%).

2-*Nitro*-NN'-*dicarbethoxybenzidine*.—The reaction between 2-nitro benzidine (5 g.) and ethyl chloroformate (10 g.) began spon taneously and was completed by heating for 10 minutes at 90—100° in presence of 20 c.c. of rectified spirit. The product (6 g.) after treatment with water crystallised from rectified spirit in orange, irregular, spear-shaped plates, m. p. 187—188° (Found : N, 10·9. $C_{18}H_{21}O_6N_3$ requires N, 11·0%).

2 : 2'-*Dinitro*-NN'-*dicarbethoxybenzidine*.—This compound was readily formed, but less readily than the preceding one (heating for 1 hour). It formed a microcrystalline, yellow powder, m. p. 200— 201° (Found : N, 13·7. Calc. : N, 13·3%).

2 : 3'- *and* 3 : 3'-*Dinitro*-NN'-*dicarbethoxybenzidines*.—The appro priate dinitrobenzidines did not react with ethyl chloroformate

ıder the above conditions. In each case, therefore, 1·5 g. of nitro-base were heated with 2 c.c. of the ester, heating being ntinued for 2 hours at 120°, and for 6 hours at 140°, in the case of e 2 : 3′- and the 3 : 3′-compound, respectively.

2 : 3′-*Dinitro*-NN′-*dicarbethoxybenzidine* formed bunches of needles, . p. 158°, from hot dilute acetic acid (Found : N, 13·5%).

3 : 3′-*Dinitro*-NN′-*dicarbethoxybenzidine* formed yellow crystals m acetic acid; m. p. 216—217° (not depressed by the addition the product of dinitrating the parent urethane).

4-*Chloro*-4′-*nitrodiphenyl*.—4-Nitrodiphenyl containing a little ınnic iodide was chlorinated at a temperature just above its p. After the calculated increase in weight had occurred, the oduct became a pasty mass on cooling. It was stirred with ohol, and the almost colourless solid was then crystallised from ıcial acetic acid. It formed pale yellow needles, m. p. 157—8°, and was identified as follows. Nitration at the ordinary nperature with nitric acid (*d* 1·5) gave a product which, after ng crystallised from glacial acetic acid, melted at 153—154°. is reacted with piperidine to give 2 : 3′ : 4-trinitro-4′-piperidinohenyl (Le Fèvre and Turner, J., 1926, 2041).

3-*Nitrobenzidine*.—4-Acetamidodiphenyl (111 g.) was obtained acetylating the crude product from the reduction of 160 g. of ıitrodiphenyl, iron powder, water, and ferric chloride being used. e acetamido-compound was found to nitrate better by the lowing method than by that mentioned by Scarborough and aters (J., 1927, 1133).

The acetamido-compound (21 g.) was slowly added to a mixture 200 c.c. of nitric acid (*d* 1·5) and 100 c.c. of glacial acetic acid, temperature being kept below 20°. After 5 minutes, the ution was poured into water, and the precipitate was crystallised m much acetic acid.

The dinitro-compound so obtained was hydrolysed by dissolving in concentrated sulphuric acid, adding water until separation of id occurred, and then heating at 125° for ½ hour. The solution s then diluted and filtered, and the whole of the crude base luced as follows :

A suspension of base (25 g.) in 250 c.c. of rectified spirit and) c.c. of concentrated aqueous ammonia was boiled under reflux, l a current of hydrogen sulphide passed through it. Aqueous ımonia was added from time to time. After 1 to 1·5 hours, all the ıpended solid dissolved, and was replaced by a red, crystalline ecipitate. This was filtered off and crystallised from alcohol eld, 13 g.). Its m. p., 208—210°, was not affected by further stallisation (Found : N, 19·5. $C_{12}H_{11}O_2N_3$ requires N, 18·3%).

3-Nitrobenzidine forms very characteristic, chocolate-brown leaflets with a coppery reflex, and is almost insoluble in alcohol.

The *diacetyl* derivative was prepared by adding 8 c.c. of acetic anhydride to a boiling solution of 2 g. of the base in 40 c.c. of glacial acetic acid. After ½ hour, water was added until precipitation began. On cooling slowly, yellow needles separated, m. p. 249—250°. The diacetyl derivative was added to nitric acid (*d* 1·5) at 0°, the solution added to excess of water, and the product hydrolysed in the usual manner. The base obtained was identical with 3 : 3′-dinitrobenzidine.

4-Chloro- and 4-Bromo-4′-phthalimidodiphenyl.—These were obtained by heating with phthalic anhydride (160—170°; 2 hours) the crude products resulting from the iron–water–ferric chloride reduction of 4-chloro- and 4-bromo-4′-nitrodiphenyl, respectively. The *chloro-* and the *bromo*-derivative both form pale yellow needles from *cyclo*hexanol and melt at 245° and 260°, respectively.

Nitration of 4-Chloro-4′-phthalimidodiphenyl.—To a suspension of 18 g. of the chloro-compound in 100 c.c. of nitric acid (*d* 1·4) were added 150 c.c. of nitric acid (*d* 1·5), the temperature being maintained below 15°. The solution was poured into water, and the precipitate collected and dried. It was dissolved in a mixture of 150 c.c. of concentrated sulphuric acid and 10 c.c. of water, and the solution was heated at 130—140° for 10 minutes and then gradually diluted. The resulting crude base (18 g.) was treated with 400 c.c. of boiling alcohol. The undissolved portion (7·5 g.) had m. p. 190—200°, and after crystallisation from glacial acetic acid, m. p. 213°. This product was identical with 4-chloro-2 : 3′-dinitro-4′-aminodiphenyl (Le Fèvre and Turner, *loc. cit.*). The filtrate from the 7·5 g. of residue yielded a product which could not be purified by crystallisation, but was converted into 2 : 3′-dinitrobenzidine when it was heated at 160—180° in a sealed tube for 7 hours with alcoholic ammonia. Thus, 18 g. of chlorophthalimido-compound gave 7 g. of 4-chloro-2 : 3′-dinitro-4′-aminodiphenyl and 5 g. of 2 : 3′-dinitrobenzidine (after crystallisation from phenol–alcohol).

Nitration of 4-Bromo-4′-phthalimidodiphenyl.—Nitration was carried out in the manner described for the chloro-compound. From the mixed crude hydrolysis product, only 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl was obtained after replacement of the amino-groups by bromine atoms (perbromide method).

Preparation of NN′-Dicarbamylbenzidine.—No details for the preparation are given in the literature; *e.g.*, Schiff (*loc. cit.*) merely "heated carbamide with benzidine."

When benzidine (1 mol.) was heated at 140—145° in three different experiments with 1, 2, and 3 mols. of carbamide, respectively, until

ammonia was no longer evolved, and the cooled products were exhaustively extracted with boiling alcohol, the three condensations gave 41, 85, and 85%, respectively, of the theoretically obtainable quantity of dicarbamylbenzidine.

The preparation of this substance is most conveniently carried out by rapidly evaporating an alcoholic solution containing benzidine (1 mol.) and carbamide (2 mols.), transferring the finely divided, intimate mixture so obtained into a number of boiling tubes, and heating these in a bath kept at 140—145°. Evolution of ammonia at once occurs, and when it has ceased, the resulting hard grey masses are extracted with alcohol as before. The dicarbamylbenzidine so obtained, after being dried at 120°, forms a light grey or almost white powder, insoluble in all common solvents, and not melting below 300°.

The dicarbamyl compound is also readily obtainable by slowly treating a solution of 5·1 g. of benzidine hydrochloride in 300 c.c. of water with one of 1·7 g. of potassium cyanate in 100 c.c. of water. After 4 hours, the precipitate is collected, and purified as described above.

Colour reactions with nitrous and with nitric acid. Two 0·02% solutions in concentrated sulphuric acid were prepared: (A) Dicarbamylbenzidine, and (B) potassium nitrate. Measured volumes of B were diluted with 10, 20, 30, etc., volumes of concentrated sulphuric acid. One c.c. of A was added to 10 c.c. of diluted solutions of B. One c.c. of B diluted by 100, 150, and 200 c.c. of sulphuric acid, respectively, gave a rich port-wine colour, a pale reddish-purple colour, and a very faint pink colour, respectively. Addition to the most dilute solution of a few drops of stock diphenylamine solution (in dilute sulphuric acid) caused the development of a marked blue colour. From these results it is seen that *dicarbamylbenzidine will detect 1 g. of potassium nitrate with certainty in the presence of 500,000 c.c. of sulphuric acid.* If large volumes are used, the colour is visible at 1·5 times this dilution.

A solution of sodium nitrite (0·005 g.) in 25 c.c. of concentrated sulphuric acid was treated with 1 c.c. of A. No coloration was produced. When 0·1 c.c. of B was added, a bluish-purple colour at once developed.

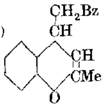
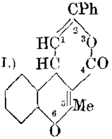
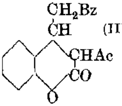
One of us (R. J. W. Le F.) is indebted to the Advisory Committee of the Department of Scientific and Industrial Research for a maintenance grant, and to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

East London College,
University of London. [*Received, November 9th, 1927.*]

XXXVI.—*The Condensation of Certain β-Ketonic Esters with* o-*Hydroxymonostyryl Ketones.*

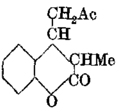
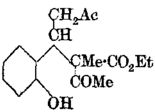
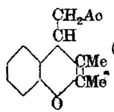
By Rowland Hill.

It has been shown (Heilbron and Hill, J., 1927, 918) that, contrary to the findings of Forster and Heilbron (J., 1924, **125**, 340), the sole reaction products of the condensation of ethyl acetoacetate with phenyl 2-hydroxystyryl ketone under various conditions are 4-phenacyl-2-methyl-1 : 4-benzopyran (I) and 2-phenyl-5-methyl-3 : 4-coumalo-6-benzopyran (II). The failure to isolate 3-acetyl-4-

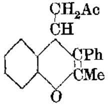
(I.)  (II.)  (III.) 

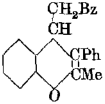
phenacyldihydrocoumarin (III) has led to the investigation now described, in which the interaction of certain α-substituted β-ketonic esters with *o*-hydroxymonostyryl ketones has been examined with a view to determine whether dihydrocoumarin ring formation is possible under such conditions.

The interaction of ethyl methylacetoacetate with 2-hydroxystyryl methyl ketone was first studied, as it was considered that the introduction of a methyl group into the β-ketonic ester would tend to prevent γ-pyran ring formation and result in the formation of 4-acetonyl-3-methyldihydrocoumarin (IV). This, however, did not prove to be the case, for the substance actually isolated from the reaction mixture had an empirical formula $C_{14}H_{16}O_2$, which corresponds to the loss of the carbethoxyl group and one molecule of water from the primary additive product (V). A consideration of the structure of the latter clearly shows that water can only have been eliminated by a prior hydrolysis of the carbethoxyl group, followed by loss of carbon dioxide. γ-Pyran formation then ensues in the normal manner to yield 4-*acetonyl*-2 : 3-*dimethyl*-1 : 4-*benzopyran* (VI). In a similar manner, phenyl 2-hydroxystyryl ketone yielded 4-*phenacyl*-2 : 3-*dimethyl*-1 : 4-*benzopyran*.

(IV.)  (V.)  (VI.) 

The condensation of ethyl phenylacetoacetate with *o*-hydroxymonostyryl ketones was next investigated, since it was thought that the substitution of the phenyl group for the methyl radical of the β-ketonic ester might influence the reaction in favour of dihydrocoumarin ring formation. The reaction, however, followed the normal course, yielding 4-*acetonyl*-3-*phenyl*-2-*methyl*-1 : 4-*benzopyran* (VII) and 4-*phenacyl*-3-*phenyl*-2-*methyl*-1 : 4-*benzopyran* (VIII).

(VII.) 

 (VIII.)

The study of these condensations was also extended so as to include ethyl oxalacetate, ethyl cyanoacetate, and ethyl malonate, but, strangely enough, no evidence has as yet been adduced of the addition of these esters to an ethenoid linkage containing an *o*-hydroxyl group. Even under the most drastic conditions the ketone has been recovered unchanged. The failure to isolate an additive product is surprising when it is considered that ethyl cyanoacetate and ethyl malonate are in a general way more reactive than ethyl acetoacetate.

The reaction between ethyl malonate and phenyl 2-hydroxystyryl ketone was studied exhaustively. After the reactants had been kept in concentrated sodium ethoxide solution at room temperature for 10 weeks, coumarin-α-carboxylic acid was isolated. Normal addition at the ethenoid linkage had therefore been superseded by scission of the ketone in the presence of alkali, with formation of acetophenone and salicylaldehyde, and the latter had then condensed with ethyl malonate in the normal manner (Stuart, J., 1886, **49**, 366). This is reminiscent of a case observed by Vorländer (*Annalen*, 1896, **294**, 334), who found that the condensation of ethyl malonate with 4-methoxystyryl *iso*propyl ketone in presence of alcoholic sodium ethoxide resulted in considerable quantities of *p*-methoxycinnamic acid being formed.

EXPERIMENTAL.

4-*Acetonyl*-2 : 3-*dimethyl*-1 : 4-*benzopyran* (VI).—2-Hydroxystyryl methyl ketone (5 g.) dissolved in the minimum quantity of absolute alcohol (distilled over calcium), containing ethyl methylacetoacetate (7·5 g.), was treated with sodium ethoxide (from 1·7 g. of sodium) in alcohol (25 c.c.), and the homogeneous, red solution kept at room temperature for 8 days; it became lighter in colour and a small

quantity of sodium carbonate was deposited. After removal of the latter, the mixture was gradually diluted with water; long, colourless needles then separated. Recrystallised three times from aqueous alcohol, the pyran was obtained (yield, 3·5 g.) in large, colourless plates, m. p. 141°. It is almost insoluble in cold aqueous alkali, but dissolves readily on warming. With concentrated sulphuric acid it develops a yellow coloration (Found: C, 77·9; H, 7·7. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%).

4-*Phenacyl*-2 : 3-*dimethyl*-1 : 4-*benzopyran* was prepared in a similar manner from phenyl 2-hydroxystyryl ketone. The filtrate, after removal of sodium carbonate, was diluted with water, the viscous, brown oil which separated was taken up in ether, and the moist ethereal solution vigorously scratched. A dark yellow solid was slowly deposited which, when pressed on a porous tile to remove adherent oily matter and recrystallised repeatedly from benzene, in which it was but moderately soluble, formed minute, colourless needles, m. p. 179° (Found: C, 81·8; H, 6·5. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

4-*Acetonyl*-3-*phenyl*-2-*methyl*-1 : 4-*benzopyran* (VII).—A hot solution containing 2-hydroxystyryl methyl ketone (8·1 g.), absolute alcohol (40 c.c.), and ethyl phenylacetoacetate (12 g.) was treated with alcoholic sodium ethoxide (2·6 g. of sodium). The mixture, which immediately assumed a deep red colour, was kept at room temperature for 3 days. After decanting from deposited sodium carbonate, the clear solution was slowly diluted with water; rosettes of slender needles contaminated with a brown, viscous oil then slowly separated. These were recrystallised from glacial acetic acid and finally from acetone, from which the pure substance was deposited in long, colourless needles, m. p. 186—187°. It is sparingly soluble in hot or cold aqueous alkali, but dissolves in concentrated sulphuric acid to a pale yellow solution (Found: C, 81·7; H, 6·4. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

4-*Phenacyl*-3-*phenyl*-2-*methyl*-1 : 4-*benzopyran* (VIII).—A mixture of phenyl 2-hydroxystyryl ketone (7 g.), absolute alcohol (50 c.c.), and ethyl phenylacetoacetate (7·5 g.) was treated with alcoholic sodium ethoxide (1·6 g. of sodium), and the red solution kept at room temperature for 6 days. On dilution with water, a dark, viscous oil slowly separated, which was dissolved in acetone and the solution vigorously scratched. A red, amorphous solid was thus deposited, which was repeatedly crystallised from acetone in the presence of blood-charcoal. When pure, the compound separated in colourless prisms, m. p. 219—221° (with preliminary darkening). It is sparingly soluble in the usual organic solvents with the exception of chloroform and pyridine, insoluble in hot

aqueous alkali, and gives a pale yellow coloration with concentrated sulphuric acid (Found : C, 84·9; H, 6·0. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%).

Condensation of Ethyl Malonate with Phenyl 2-Hydroxystyryl Ketone.—Phenyl 2-hydroxystyryl ketone (10 g.) and ethyl malonate (11 g.) were dissolved in the minimum quantity of absolute alcohol and treated with alcoholic sodium ethoxide (from 3 g. of sodium). The homogeneous, red solution was kept at room temperature for 10 weeks, an amorphous, red solid slowly separating. This was collected and thoroughly washed with dilute hydrochloric acid and finally with water. The dried product crystallised from benzene (with blood-charcoal) in long, colourless needles, m. p. 190°. The melting point of coumarin-α-carboxylic acid ascribed by various authors varies between 187° and 191° (Found : C, 62·6; H, 5·3. Calc. for $C_{10}H_6O_4$: C, 62·6; H, 5·3%).

The author desires to express his thanks to Professor I. M. Heilbron, D.S.O., for his criticism and advice, and also to the United Alkali Co., Ltd., for a grant which enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, September 16th, 1927.*]

XXXVII.—*The Hydrogen-ion Concentration of Aqueous Iodine Solutions.*

By HARRY MEDFORTH DAWSON.

THE use of iodine solutions in the study of the dynamics of autocatalysed reactions of the keto–enol type has directed attention to the question of the hydrogen-ion concentration of such solutions. Apart from this particular application, the problem is of interest in that the p_H value of aqueous solutions which contain iodine and iodide cannot be determined directly by the usual methods. Their nature precludes the use of the hydrogen-electrode and indicator methods, and the measurement of electrical conductivity can only be applied to iodide-free solutions of iodine. It is possible that the glass-electrode method could be employed, but the results obtained with this in the case of other solutions appear to be somewhat erratic.

The object of this paper is to show how the p_H value may be derived indirectly from a consideration of the equilibria which are involved in the interaction of iodine, potassium iodide, and

water. The equilibria in question for freshly prepared solutions * are

$$I_2 + H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{I} + HIO \quad . \quad . \quad . \quad . \quad (1)$$

$$H_2O \rightleftharpoons \overset{+}{H} + \overset{-}{O}H \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$I_2 + \overset{-}{I} \rightleftharpoons \overset{-}{I_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for which the respective constants at 25° are

$$K_1 = [\overset{+}{H}][\overset{-}{I}][HIO]/[I_2] = 6 \times 10^{-13} \quad . \quad . \quad . \quad (4)$$

$$K_w = [\overset{+}{H}][\overset{-}{O}H] = 10^{-14} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\text{and } K_2 = [I_2][\overset{-}{I}]/[\overset{-}{I_3}] = 1{\cdot}38 \times 10^{-3} \quad . \quad . \quad . \quad . \quad (6)$$

The constant K_1 is based on the determination by Bray (*J. Amer. Chem. Soc.*, 1910, **32**, 932) of the electrical conductivity of a saturated solution of iodine in pure water; K_w is the ionic product for water; and K_2 is derived from experiments on the distribution of iodine between iodide solutions and a non-aqueous medium immiscible with water (compare Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19). Although the reaction between the halogens and water is commonly referred to as a hydrolytic process, there is an obvious similarity between the production of hydrogen ions in this way and by the dissociation of an acid. The dissolved halogen behaves indeed like a weak acid, and the p_H value of iodine–iodide solutions is determined by the joint effect of the hydrion-producing processes which are represented by equations (1) and (2). The relative importance of the two reactions depends on the concentration of the free iodine in the solution, and this in turn depends on the concentration of the iodide.

In essence, the problem under consideration may be said to resemble very closely that which is involved in the determination of the hydrogen-ion concentration of a solution which contains two weak acids. If the concentrations of the two weak acids HA_1 and HA_2 are C_1 and C_2, and the corresponding ionisation constants are K' and K'', we have in accordance with the mass law

$$[\overset{-}{A_1}] = K'C_1/[\overset{+}{H}] \text{ and } [\overset{-}{A_2}] = K''C_2/[\overset{+}{H}]$$

$$\text{and since} \quad [\overset{+}{H}] = [\overset{-}{A_1}] + [\overset{-}{A_2}] = [K'C_1 + K''C_2]/[\overset{+}{H}]$$

we obtain $[\overset{+}{H}] = \sqrt{K'C_1 + K''C_2}$, which gives the hydrogen-ion concentration of the solution containing the two acids.

* On keeping, iodic acid is formed (compare Sammet, *Z. physikal. Chem.* 1905, 53, 687), but the effect of this has not been considered in the calculations.

In applying a similar procedure to the determination of the hydrogen-ion concentration of iodine–iodide solutions, the total concentrations of the iodide and iodine will be denoted by a and b, respectively. If then x represents the molar concentration of the free iodine, the concentration of the tri-iodide ion is given by $(b - x)$ and that of the iodine ion by $(a - b + x)$. The equilibrium constant K_2 may then be written $K_2 = x(a - b + x)/(b - x)$, from which $2x = \sqrt{(K_2 + a - b)^2 + 4K_2b} - (K_2 + a - b)$, and this enables us to calculate the concentration of the free iodine in the solution.

Denoting the concentration of the hydrogen ion derived from the hydrolysis of iodine by $[\overset{+}{H}]_1$, and that derived from the ionisation of water by $[\overset{+}{H}]_2$, we obtain from equations (4) and (5)

$$[\overset{+}{H}]_1 = [HIO] = K_1[I_2]/[\overset{-}{I}][\overset{+}{H}]$$

and

$$[\overset{+}{H}]_2 = [O\overset{-}{H}] = K_w/[\overset{+}{H}]$$

in which $[\overset{+}{H}] = [\overset{+}{H}]_1 + [\overset{+}{H}]_2$ is the total concentration of the hydrogen ion. From the above we derive

$$[\overset{+}{H}]_1/[\overset{+}{H}]_2 = K_1[I_2]/K_w[\overset{-}{I}] = K_1x/K_w(a - b + x) \quad . \quad (7)$$

which gives the relative quantities of hydrogen ions resulting from the two proton-producing processes. Furthermore, we obtain

$$[\overset{+}{H}]_1/[\overset{+}{H}] = [K_1x/(a - b + x)]/[K_w + K_1x/(a - b + x)] \quad (8)$$

$$[\overset{+}{H}]_2/[\overset{+}{H}] = K_w/[K_w + K_1x/(a - b + x)] \quad . \quad . \quad (8a)$$

and

$$[\overset{+}{H}] = \sqrt{K_w + K_1x/(a - b + x)} \quad . \quad . \quad . \quad . \quad (9)$$

Table I gives a series of numbers which have been calculated from the foregoing equations. It shows the variation in the hydrogen-ion concentration of a series of solutions which contain a fixed quantity of total iodine ($b = 0{\cdot}002$ mol. per litre) and variable quantities of potassium iodide. (The choice of this particular iodine concentration was determined by the circumstance that information in regard to these solutions was required for other purposes.) Col. 1 gives the molar concentration of potassium iodide; col. 2 the molar concentration of the free iodine; col. 3 the proportion of the total hydrogen-ion concentration which is due to hydrolysis of the iodine; col. 4 the total hydrogen-ion concentration of the solutions; and col. 5 the corresponding p_H value.

TABLE I.

p_H values of iodine–iodide solutions containing 0·002 mol. of iodine per litre.

a.	$x \times 10^3$.	$[\overset{+}{H}]_1/[\overset{+}{H}]$.	$[H] . 10^7$.	p_H.*
0·001	1·48	0·995	13·6	5·86
0·002	1·11	0·985	7·8	6·11
0·004	0·680	0·94	4·0	6·40
0·006	0·472	0·86	2·7	6·57
0·015	0·189	0·46	1·35	6·87
0·02	0·140	0·315	1·20	6·92
0·05	0·056	0·065	1·05	6·98

* According to Bray's conductivity measurements, the p_H value of an iodide-free saturated aqueous solution of iodine is 5·0.

From the above table it is apparent that the p_H value of solutions which contain a fixed amount of iodine increases with the concentration of the potassium iodide and approaches asymptotically to the limiting value $p_H = 7·00$ when the iodide is present in large excess. This relation is directly connected with the circumstance that the concentration of the free iodine in the solution tends towards a zero limiting value.

Table II shows the variation of p_H for a series of solutions for which the ratio of iodine to iodide is constant whilst the absolute concentration is varied. The results show that the dilution of such a solution is associated with a diminution of the p_H value.

TABLE II.

p_H values of iodine solutions for which $[KI]/[I_2] = 2·0$.

a.	$x . 10^3$.	$[\overset{+}{H}]_1/[\overset{+}{H}]$.	$[\overset{+}{H}] . 10^7$.	p_H.†
0·0004	0·158	0·965	5·2	6·28
0·004	0·68	0·94	4·0	6·40
0·01	0·94	0·90	3·25	6·47
0·05	1·25	0·74	1·95	6·71
0·20	1·23	0·43	1·32	6·88

† It may be shown that the p_H value of this series of solutions approximates with increasing dilution to a limiting value of $p_H = 6·25$. This value assumes that $[\overset{-}{I}]$ is not affected by the hydrolysis of the free iodine. The ultimate limiting value is of course $p_H = 7·00$.

It should be recognised that the p_H values recorded in the above tables are based on the number which has been recorded by Bray for the constant K_1 for the hydrolytic equilibrium and therefore refer only to freshly prepared solutions.

The method of procedure for the derivation of p_H remains the same if the iodine–iodide solutions contain small quantities of carbonic acid or other very weak acid. Denoting the concentration

of such a weak acid HA by C and its ionisation constant by K_a, we have the following relations:

$$[\overset{+}{\mathrm{H}}] = [\mathrm{HIO}] + [\mathrm{O}\overset{-}{\mathrm{H}}] + [\overset{-}{\mathrm{A}}]$$

$$[\mathrm{HIO}] = K_1x/(a - b + x)[\overset{+}{\mathrm{H}}]$$

$$[\mathrm{O}\overset{-}{\mathrm{H}}] = K_w/[\overset{+}{\mathrm{H}}]$$

$$[\overset{-}{\mathrm{A}}] = K_aC/[\overset{+}{\mathrm{H}}]$$

whence $$[\overset{+}{\mathrm{H}}] = \sqrt{K_aC + K_w + K_1x/(a - b + x)} \quad . \quad . \quad (10)$$

If the product K_aC is of the same order of magnitude as $K_1x/(a + b - x)$, the p_{H} value of the solution will of necessity be determined *jointly* by the ionisation of the acid HA and the hydrolysis of the iodine.

Observations on the initial velocity of certain acid-catalysed reactions in iodine–iodide solutions have given results which suggest that the actual variations in p_{H} are in general agreement with the changes indicated by the data in the tables.

Summary.

The hydrogen-ion concentrations of aqueous solutions of iodine have been calculated.

For a fixed concentration of iodine, they fall with increase in the amount of iodide present.

For solutions with a fixed ratio $[\mathrm{KI}]/[\mathrm{I_2}]$, they increase with the dilution.

THE UNIVERSITY, LEEDS. [*Received, November 17th,* 1927.]

XXXVIII.—*The Parachor and Chemical Constitution. Part VII. Further Examples of Semipolar Double Bonds.*

By ADOLPH FREIMAN and SAMUEL SUGDEN.

(1) *Sulphones.*

THE work described in this paper was designed, in the first place, to determine more accurately the effect upon the parachor of the semipolar double bond. It has been shown in Part I (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525) that the constant for this structure is about $-1{\cdot}6$ units. Some of the substances there studied are, however, difficult to purify, and this value of the constant is of the same order of magnitude as the experimental

error. We have therefore studied a number of sulphones and related substances of the type which contain this structure, since these substances can readily be purified by crystallisation and have convenient melting points. The parachors calculated from the surface tension and density of the fused substances are collected in Table I in the column headed "[*P*] obs." The next column gives the sum of all the atomic and structural constants except that for the semipolar double bond; by subtracting this sum from [*P*] obs., one obtains the figures given in the last column, which represent the effect of this structure upon the parachor. It will be seen that the data for these five carefully purified substances lead to a value for the constant sought of $-1{\cdot}6$ units, which is identical with the figure obtained in the earlier investigation (*loc. cit.*).

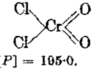
TABLE I.

Substance.	[*P*] obs.	Σ[*P*].	Semipolar double bond.
p-Toluenesulphonyl chloride	367·8	371·6	$-1{\cdot}9 \times 2$
Ethyl *p*-toluenesulphonate	431·8	432·4	$-0{\cdot}3 \times 2$
Benzylmethylsulphone	369·8	373·4	$-1{\cdot}8 \times 2$
Diphenylsulphone	465·7	468·3	$-1{\cdot}3 \times 2$
Phenylbenzylsulphone	503·5	507·3	$-1{\cdot}9 \times 2$
		Mean	$-1{\cdot}6$

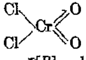
It is therefore concluded that the semipolar double bond has a small but real negative effect upon the parachor. This may be explained, as suggested in the earlier investigation, by a small contraction in volume due to the electrostatic attraction between the oppositely charged atoms which are joined by this linkage.

(2) Chromium Compounds.

Measurements have also been made of the surface tension and density of chromyl chloride, from which the parachor of this substance is found to be 199·1. From this observation the parachor for chromium can be calculated on the assumption that the oxygen atoms are held (*a*) by non-polar double bonds (I), or (*b*) by semipolar double bonds (II). The first hypothesis leads to an inadmissible

(I.) 

Σ[*P*] = 195·0.
Cr = 4·1.

 (II.)

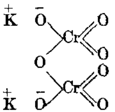
Σ[*P*] = 145·4.
Cr = 53·7.

value (4·1) for the parachor for chromium (the smallest atomic parachor yet found is C = 4·8), whilst the second hypothesis give the more reasonable figure of 53·7, which is compatible with th

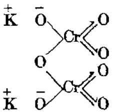
values found for neighbouring elements in the periodic table, *e.g.*, S = 48·2, Se = 58.*

Further evidence in support of this value can be obtained from the measurements of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1) of the surface tension and density of fused potassium dichromate, from which [*P*] obs. = 451. This figure can *only* be regarded as a rough value, since the parachor shows a decided drift with temperature (see Experimental). From Jaeger's data for the alkali halides and sulphates, which will be discussed more fully in a later paper, the parachor of potassium is found to be 106. By the use of this figure, the parachor for chromium in potassium dichromate becomes 4·5 if the oxygen atoms are held by non-polar double bonds (III), and 54 if these linkages are of the semipolar type (IV). In these calculations the polar bond between potassium and oxygen has been assigned a value of − 1·6 units. Indirect evidence for this figure has been advanced in Part V of this series (Sugden, J., 1927, 1173), and direct evidence from measurements on fused salts has now been obtained and will be discussed in a later paper.

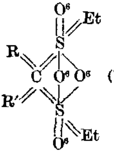
For both of these substances the octet theory predicts that the double bonds holding the oxygen atoms must be semipolar; hence the data discussed above give experimental support to the view that in these compounds of chromium the octet is not exceeded. This is of particular interest, since chromium belongs to the first long period and is a transition element.

(III.) 

Σ[*P*] = 442.
Cr = 4·5.

 (IV.)

Σ[*P*] = 342.
Cr = 54·5.

 (V.)

Δ[*P*] = −23·2.

(3) β-*Disulphones. An Anomaly.*

In addition to the simple sulphones referred to in Table I, two β-disulphones were also examined, *viz.*, sulphonal and trional, and were found to exhibit the large anomaly shown in Table II. These anomalies are not due to impurities, for the specimens examined had sharp melting points which were unchanged by crystallisation from a number of solvents. Nor are they due to errors of observation, for check measurements made by another observer in this

* Deduced from measurements on selenium compounds to be described in a later paper of this series.

laboratory, using different instruments, gave substantially the same values for the surface tension and density of trional.

TABLE II.

Substance.	Formula.	[P] obs.	[P] calc.	Anomaly.
Sulphonal	$CMe_2(SO_2Et)_2$	465·5	477·2	−11·7
Trional	$CMeEt(SO_2Et)_2$	493·8	516·2	−22·4

The close agreement between the observed and calculated values of the parachor for the simple sulphones (Table I) and for a number of other sulphur compounds described in Part I (*loc. cit.*) of this series is convincing evidence that the constant assigned to sulphur (48·2) is substantially accurate, and that the additive character of the parachor persists in sulphur compounds of this type. It is evident, therefore, that the β-disulphones must contain some special structure which is not expressed by their formula and is not present in the simple sulphones.

It may be noted at once that this new structure cannot be the conversion of the semipolar into non-polar double bonds, for such a change would give a large increase in the parachor, whereas the anomaly found is negative. Moreover, since the only structure which has so far been found to have a large negative parachor is the singlet linkage (Sugden, J., 1927, 1173), it seems probable tha there is some *interaction between the two SO_2 groups by which singlet linkages are formed.* *We intend to examine other disulphones* and similar compounds to obtain further evidence; meanwhile, we suggest as a tentative explanation that these substances are tautomeric, one individual having the structure represented by the usua formula, and the other having the electronic structure (V). Th larger anomaly exhibited by trional may then be accounted for b the well-known effect of bulky substituents in stabilising rin structures. For formula (V) the structural constant would b obtained as follows:

2 Four-membered rings,	$2 \times 11·6$	=	+23·2
2 Semipolar double bonds,	$2 \times -1·6$	=	− 3·2
4 Semipolar single bonds,	$4 \times -12·4$	=	−49·6
			−29·6

For the disulphone formula, the structural constant is that f 4 semipolar double bonds or $4 \times -1·6 = -6·4$. Comple transformation to the structure represented by (V) would therefo give an anomaly of −23·2; hence, on this view trional is large composed of the cyclic isomeride.

EXPERIMENTAL.

In the course of this investigation measurements have been ma of the surface tension and density of *p*-toluenesulphonyl chlori

ethyl *p*-toluenesulphonate, benzylmethylsulphone, diphenylsulphone, phenylbenzylsulphone, chromyl chloride, sulphonal, and trional. Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). The constants for the bubblers used were :—

Apparatus.	4d.	10.	15b.	16a.
r_2 (cm.)	0·139	0·166	0·178	0·179
A	0·007767	0·004311	0·00945	0·008272

Densities were determined by means of the U-shaped pyknometer described previously (J., 1924, **125**, 1171), except in the case of chromyl chloride, for which a sealed bulb was used to avoid exposure to the atmosphere.

The tables below are set out in the same manner as in earlier papers of this series and do not need further description. The parachor is calculated by the usual formula, *d*, which is very small for all the substances now studied, being neglected.

p-*Toluenesulphonyl chloride*, $C_7H_7{\cdot}SO_2Cl$, $M = 190{\cdot}5$, was recrystallised from benzene and melted sharply at 68° (corr.). Densities determined: $D_{4^\circ}^{76^\circ} = 1{\cdot}261$, $D_{4^\circ}^{97{\cdot}5^\circ} = 1{\cdot}237$, $D_{4^\circ}^{138^\circ} = 1{\cdot}201$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}333 - 0{\cdot}000961t$.

App.	*t*.	*P*.	*D*.	ϕ.*	γ.	Parachor.
16a	74	4143	1·262	1·0369	35·54	368·6
,,	103·5	3697	1·233	1·0404	31·82	367·0
						Mean 367·8

* A correction factor, see J., 1924, **125**, 31.

Ethyl p-*toluenesulphonate*, $C_9H_{12}O_3S$, $M = 200{\cdot}1$, was recrystallised from ethyl acetate and melted at 33—34° (corr.). Densities determined: $D_{4^\circ}^{47^\circ} = 1{\cdot}166$, $D_{4^\circ}^{58{\cdot}5^\circ} = 1{\cdot}157$, $D_{4^\circ}^{70^\circ} = 1{\cdot}145$, $D_{4^\circ}^{89^\circ} = 1{\cdot}130$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}206 - 0{\cdot}000862t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
10	40	9290	1·172	1·0142	40·62	430·9
,,	53·5	8961	1·160	1·0145	39·18	431·5
,,	70	8597	1·146	1·0150	37·62	432·3
,,	83	8255	1·134	1·0154	36·14	432·6
						Mean 431·8

Benzylmethylsulphone, $C_8H_{10}O_2S$, $M = 170{\cdot}1$, was recrystallised from benzene and melted at 124·5° (corr.). Densities determined: $D_{4^\circ}^{129^\circ} = 1{\cdot}140$, $D_{4^\circ}^{142{\cdot}5^\circ} = 1{\cdot}128$, $D_{4^\circ}^{163^\circ} = 1{\cdot}112$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}246 - 0{\cdot}000825t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
15b	142·5	3665	1·128	1·0371	35·92	369·2
,,	164·5	3458	1·110	1·0387	33·93	369·8
,,	184	3278	1·094	1·0403	32·22	370·3
						Mean 369·8

Diphenylsulphone, $C_{12}H_{10}O_2S$, $M = 218{\cdot}1$, was recrystallised from benzene and melted at 125° (corr.). Densities determined : $D_{4°}^{141{\cdot}5°} = 1{\cdot}157$, $D_{4°}^{161°} = 1{\cdot}142$, $D_{4°}^{172°} = 1{\cdot}133$, $D_{4°}^{183°} = 1{\cdot}126$, whence $D_{4°}^{t°} = 1{\cdot}267 - 0{\cdot}000774t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
15b	137·5	3857	1·161	1·0363	37·77	465·6
,,	157	3668	1·145	1·0376	35·97	466·5
,,	179·5	3400	1·128	1·0400	33·42	465·0
					Mean	465·7

Phenylbenzylsulphone, $C_{13}H_{12}O_2S$, $M = 232{\cdot}2$, was recrystallised from alcohol and melted at 146° (corr.). Densities determined : $D_{4°}^{153°} = 1{\cdot}126$, $D_{4°}^{164°} = 1{\cdot}116$, $D_{4°}^{173{\cdot}5°} = 1{\cdot}108$, $D_{4°}^{186{\cdot}5°} = 1{\cdot}098$, whence $D_{4°}^{t°} = 1{\cdot}249 - 0{\cdot}000809t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
15b	153·5	3612	1·125	1·0375	35·40	503·5
,,	184	3294	1·100	1·0402	32·38	503·6
					Mean	503·5

Chromyl chloride, CrO_2Cl_2, $M = 155{\cdot}0$, was prepared by the action of concentrated sulphuric acid on a mixture of chromic acid and concentrated hydrochloric acid, and purified by distillation : b. p. 115—116° (corr.)/758 mm. Densities determined : $D_{4°}^{15°} = 1{\cdot}937$, $D_{4°}^{24°} = 1{\cdot}920$, $D_{4°}^{30°} = 1{\cdot}910$, $D_{4°}^{39°} = 1{\cdot}893$, $D_{4°}^{49°} = 1{\cdot}873$, $D_{4°}^{60°} = 1{\cdot}855$, whence $D_{4°}^{t°} = 1{\cdot}965 - 0{\cdot}00185t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
4d	19	4532	1·930	1·0401	36·61	197·5
,,	41	4271	1·889	1·0416	34·55	198·9
,,	64	3966	1·847	1·0438	32·16	199·8
,,	78	3754	1·821	1·0456	30·48	200·0
					Mean	199·1

Potassium dichromate, $K_2Cr_2O_7$, $M = 294{\cdot}2$. The following data are taken from the work of Jaeger (*loc. cit.*).

t.	γ.	*D*.	Parachor.
420	140·1	2·271	445·6
454	139·4	2·248	449·7
480	138·4	2·229	452·9
504	137·0	2·213	454·8
		Mean	450·8

Sulphonal, $C_7H_{16}O_4S_2$, $M = 228{\cdot}2$, was repeatedly crystallised from absolute alcohol and melted at 125·8° (corr.). Densities determined : $D_{4°}^{132°} = 1{\cdot}183$, $D_{4°}^{141°} = 1{\cdot}176$, $D_{4°}^{152{\cdot}5°} = 1{\cdot}166$, $D_{4°}^{180{\cdot}5°}$ 1·145, whence $D_{4°}^{t°} = 1{\cdot}278 - 0{\cdot}000725t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
15b	132·5	3489	1·182	1·0408	34·31	467·1
,,	154·5	3268	1·166	1·0430	32·20	466·1
,,	169·5	3093	1·155	1·0450	30·54	464·4
,,	177·5	3027	1·149	1·0457	29·91	464·4
					Mean	465·5

Trional, $C_8H_{18}O_4S_2$, $M = 242{\cdot}2$, was recrystallised from absolute alcohol and melted sharply at 75° (corr.). Densities determined; $D_{4^\circ}^{88^\circ} = 1{\cdot}199$,* $D_{4^\circ}^{98^\circ} = 1{\cdot}193$, $D_{4^\circ}^{104{\cdot}5^\circ} = 1{\cdot}183$,* $D_{4^\circ}^{116{\cdot}5^\circ} = 1{\cdot}176$, $D_{4^\circ}^{128^\circ} = 1{\cdot}163$,* $D_{4^\circ}^{136^\circ} = 1{\cdot}159$, $D_{4^\circ}^{145^\circ} = 1{\cdot}150$,* $D_{4^\circ}^{157{\cdot}5^\circ} = 1{\cdot}141$, whence $D_{4^\circ}^{t^\circ} = 1{\cdot}272 - 0{\cdot}00839t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
14	88·5	3329	1·198	1·0431	35·41	493·2*
14	110	3133	1·180	1·0451	33·39	493·4*
15b	123·5	3268	1·168	1·0431	32·20	494·0
14	136·5	2902	1·157	1·0478	31·01	494·0*
15b	147	3061	1·149	1·0452	30·23	494·3
14	158	2700	1·139	1·0505	28·93	493·3*
15b	164	2899	1·134	1·0471	28·65	494·3
					Mean	493·8

* We are indebted to Mr. F. B. Garner for the observations thus marked.

Summary.

(1) The parachor constant for the semipolar double bond is found to be −1·6 from measurements on five carefully purified sulphones and related compounds. This is in good agreement with the value found in an earlier investigation.

(2) Chromyl chloride is found to contain two semipolar double bonds and potassium dichromate four such linkages. The parachor for chromium is assigned the value 54 units.

(3) Two disulphones, sulphonal and trional, give a large negative anomaly in their parachors. It is suggested that this is due to the production of a cyclic phase by the formation of singlet linkages between oxygen atoms of the SO_2 groups.

One of us (S. S.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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FETTER LANE, E.C. 4. [*Received, December* 13*th*, 1927.]

XXXIX.—*The Solution Tension of Silver in Solvents other than Water.*

By FREDERICK KARL VICTOR KOCH.

THE Nernst formula for the electrode potential of a metal against a solution of its ions, $E = RT/nF . \log_e P/p$, does not explicitly involve any property of the solvent, but there is every reason to suppose that the tendency of the metal ion to go into solution (P) will vary with the solvent, just as the solubility of any chemical substance varies in different media (Brunner, *Z. Elektrochem.*, 1905, **11**, 415;

(J., 1927, 647), its specific conductivity being $\kappa_{25^\circ} = 0{\cdot}5$—$1{\cdot}0 \times 10^{-7}$ mho. Propionitrile (B.D.H.) was purified in the same manner as the acetonitrile, and then had $\kappa_{25^\circ} = 1{\cdot}7 \times 10^{-7}$ mho.

Benzonitrile (B.D.H.) was steam-distilled, washed with aqueous sodium carbonate solution, and extracted with ether. The extract was dried over calcium chloride, filtered, and the ether removed on the steam-bath. The benzonitrile was then distilled in a vacuum, and the constant-boiling fraction (b. p. 73°/6 mm.) was kept for about 2 days over calcium chloride and then redistilled under low pressure. The distillate was shaken with a little phosphoric oxide, and after being again distilled had specific conductivity $\kappa_{25^\circ} = 0{\cdot}5 \times 10^{-7}$ mho.

Phenylacetonitrile (B.D.H.) was shaken with potassium carbonate to remove phenylacetic and hydrocyanic acids. After filtration on a Buchner funnel, it was distilled in a vacuum at 110° (b. p. 231°/760 mm.), a large first fraction being rejected in order to ensure the removal of the last traces of benzyl chloride (b. p. 126°/760 mm.). The distillate which had come over at a constant temperature was further purified in the same way as the phenylacetonitrile and then had $\kappa_{25^\circ} = 0{\cdot}5 \times 10^{-7}$ mho.

Ethyl cyanoacetate (B.D.H.) was shaken with calcium chloride for ½ hour and distilled in a vacuum at 96° (b. p. 206°/760 mm.), a large first fraction being rejected : $\kappa_{25^\circ} = 2{\cdot}5 \times 10^{-7}$ mho.

Pyridine (Hopkin and Williams's " Pure ") was dried over solid potash and distilled at atmospheric pressure (b. p. 114—115°); it was protected by soda–lime tubes : $\kappa_{25^\circ} = 1{\cdot}7 \times 10^{-7}$ mho.

Aniline (Hopkin and Williams's " Redistilled ") was dried over solid potash and distilled in a vacuum at 76° (b. p. 184·4°/760 mm.). Dry nitrogen was passed through the bubbler instead of dry air. Precautions were taken, as in the case of pyridine, to prevent contamination by atmospheric carbon dioxide. The pure aniline was colourless, and had a specific conductivity lower than that of any of the other solvents, *viz.*, $2{\cdot}5 \times 10^{-8}$ mho. This was fortunate, since the specific conductivities of the silver nitrate solutions were also exceptionally low.

Methyl alcohol (Kahlbaum) had been kept over lime for some months. It was shaken with fresh lime and distilled at atmospheric pressure first from lime and then from dry silver nitrate. It was found that standing over anhydrous copper sulphate did not improve the product : $\kappa_{25^\circ} = 1{\cdot}5 \times 10^{-6}$ mho.

Ethyl alcohol (Burrough's " Absolute ") was purified in the same way as the methyl alcohol : $\kappa_{25^\circ} = 1{\cdot}0 \times 10^{-7}$ mho.

Acetone (Hopkin and Williams's " Redistilled ") was dried over calcium chloride and distilled at atmospheric pressure over metallic

calcium which had been scraped so as to present a fresh surface: $\kappa_{25^\circ} = 1{\cdot}3 \times 10^{-6}$ mho.

The Solutions.—Solutions of three concentrations (approximately $N/10$, $N/100$, and $N/1000$) were made in water and in the non-aqueous solvent, except those in pyridine ($N/100$, $N/500$, $N/1000$, $N/2000$), aniline ($N/100$, $N/500$, $N/1000$), and acetone ($N/90$, $N/540$, $N/1000$). All the solutions were stable except those in ethyl cyanoacetate, which decomposed, giving a brown coloration and a slight white precipitate within 24 hours of preparation. The measurements with these solutions were therefore all made on one day. Silver nitrate reacts with phenylacetonitrile, forming silver cyanide, slowly at 100° but immediately at the boiling point; at room temperature, however, the reaction is negligible.

The solutions of silver nitrate in pyridine (Werner, *Z. anorg. Chem.*, 1897, **15**, 1; Abegg and Neustadt, *loc. cit.*) and aniline (Getman and Gibbons, *Amer. Chem. J.*, 1911, **46**, 117) undoubtedly contain complexes. Since these are likely to break up with dilution, only dilute solutions (below $N/100$) were used. There is, nevertheless, some uncertainty in the deduction of ionic concentrations from conductivity measurements of these solutions, although it is to be noted that Sakhanov and Grünbaum (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1794) found that the Nernst formula held for silver nitrate concentration cells when the solutions were very dilnte. Measurements in pyridine and aniline were made in spite of the uncertainties mentioned, because it was considered that on account of their ammoniacal character they would probably yield interesting results.

Apparatus, etc.—The same conductivity and *E.M.F.* apparatus was used as that described in a previous paper (J., 1927, 647). All specific conductivities (which may be considered accurate to within 0·1%) were determined at 25° (±0·01°) in spite of the fact that the *E.M.F.*'s were measured at room temperature, because (as will be seen later) it is only the *ratio* of the specific conductivities of the two solutions which is required, and this will be very nearly the same at 25° as at room temperature, as is apparent from the fact that the difference of *E.M.F.* of the cells at 25° and at room temperature is only very slight. The specific conductivities of the pure solvents have in all cases been subtracted from the observed specific conductivity of the solution.

Two electrodes were inserted into each solution, and since measurements were made with and against the standard cell, a total of 8 readings was obtained for each *E.M.F.*; the average of these values was taken. Two independent series of *E.M.F.* determinations were made with each organic solvent, fresh solutions being used and

the electrodes replated when necessary. The values given, which are the most consistent of these, may be considered accurate to within 1—2 millivolts. The convention has been adopted of giving the *E.M.F.* the same sign as the electrode in the non-aqueous solution.

In Table I are recorded the *E.M.F.* of each cell and the specific conductivity of each solution. As will be seen in the sequel, the *E.M.F.* of the cell stands in a simple relation to the ratio of the specific conductivities of the two electrode solutions, and hence the values of κ are tabulated throughout, κ_w and κ_s being the specific conductivities of the aqueous and non-aqueous solutions, respectively. In each case the three aqueous solutions ($N/10$, $N/100$, and $N/1000$) were run against non-aqueous solutions of the three dilutions (four in the case of pyridine) specified on p. 273.

TABLE I.

Pyridine.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.* (volt).
106·5	38·59	−0·453
,,	10·49	−0·492
,,	5·923	−0·503
,,	3·278	−0·509
12·46	38·59	−0·389
,,	10·49	−0·424
,,	5·923	−0·445
,,	3·278	−0·452
1·330	38·59	−0·353
,,	10·49	−0·366
,,	5·923	−0·369
,,	3·278	−0·384

Aniline.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^7$.	*E.M.F.* (volt).
107·3	33·34	−0·327
,,	10·44	−0·343
,,	6·805	−0·372
12·52	33·34	−0·259
,,	10·44	−0·283
,,	6·805	−0·299
1·357	33·34	−0·194
,,	10·44	−0·237
,,	6·805	−0·253

Acetonitrile.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^4$.	*E.M.F.*
105·3	67·78	−0·106
,,	12·99	−0·148
,,	1·849	−0·200
12·23	67·78	−0·047
,,	12·99	−0·095
,,	1·849	−0·149
1·319	67·78	+0·019
,,	12·99	−0·030
,,	1·849	−0·097

Propionitrile.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
106·8	300·5	−0·049
,,	60·45	−0·095
,,	9·365	−0·152
12·31	300·5	+0·014
,,	60·45	−0·033
,,	9·365	−0·089
1·332	300·5	+0·069
,,	60·45	+0·028
,,	9·365	−0·025

Phenylacetonitrile.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
106·7	35·20	+0·008
,,	7·575	−0·031
,,	1·061	−0·088
11·97	35·20	+0·057
,,	7·575	+0·022
,,	1·061	−0·027
1·294	35·20	+0·113
,,	7·575	+0·078
,,	1·061	+0·026

Ethyl cyanoacetate.

$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
106·5	36·44	+0·013
,,	8·122	−0·020
,,	1·407	−0·072
12·42	36·44	+0·062
,,	8·122	+0·027
,,	1·407	−0·020
1·345	36·44	+0·121
,,	8·122	+0·086
,,	1·407	+0·042

TABLE I (*cont.*).

Benzonitrile.			Methyl alcohol.		
$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*	$\kappa_w \times 10^4$.	$\kappa_s \times 10^4$.	*E.M.F.*
106·3	45·79	+0·004	105·6	38·30	+0·092
,,	9·603	−0·036	,,	7·189	+0·041
,,	2·262	−0·073	,,	1·003	+0·006
12·44	45·79	+0·058	12·41	38·30	+0·149
,,	9·603	+0·021	,,	7·189	+0·103
,,	2·262	−0·016	,,	1·003	+0·050
1·307	45·79	+0·119	1·333	38·30	+0·205
,,	9·603	+0·079	,,	7·189	+0·157
,,	2·262	+0·047	,,	1·003	+0·113

Ethyl alcohol.			Acetone.		
$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*	$\kappa_w \times 10^4$.	$\kappa_s \times 10^5$.	*E.M.F.*
105·6	107·3	+0·088	105·6	11·50	+0·104
,,	21·84	+0·054	,,	2·360	+0·067
,,	3·484	+0·000	,,	1·592	+0·045
11·97	107·3	+0·143	12·45	11·50	+0·163
,,	21·84	+0·104	,,	2·360	+0·126
,,	3·484	+0·054	,,	1·592	+0·104
1·291	107·3	+0·195	1·340	11·50	+0·223
,,	21·84	+0·161	,,	2·360	+0·185
,,	3·484	+0·114	,,	1·592	+0·163

Discussion.

When the experimental figures recorded in Table I are plotted as in Figs. 1, 2, and 3, it is found that the value of E is a linear function of $\log_{10} \kappa_w/\kappa_s$; moreover, the slopes of the different lines for each organic solvent coupled with water are nearly equal.

This general result may be put in the form $E = A \log_{10} \kappa_w/\kappa_s + B$, and Table II gives the values of the constants deduced for each case.

TABLE II.

Solvent.	*A.*	*B.*	Solvent.	*A.*	*B.*
Pyridine	−0·065	−0·352	Ethyl cyanoacetate	−0·057	0·095
Aniline	−0·065	−0·092	Benzonitrile	−0·060	0·087
Acetonitrile	−0·064	−0·091	Methyl alcohol	−0·059	0·117
Propionitrile	−0·066	−0·012	Ethyl alcohol	−0·057	0·145
Phenylacetonitrile	−0·057	+0·088	Acetone	−0·063	0·227

Now, on the basis of the Nernst theory, the *E.M.F.* of the cell $Ag|AgNO_3$(aqueous)$|AgNO_3$ (non-aqueous)$|Ag$ is given by

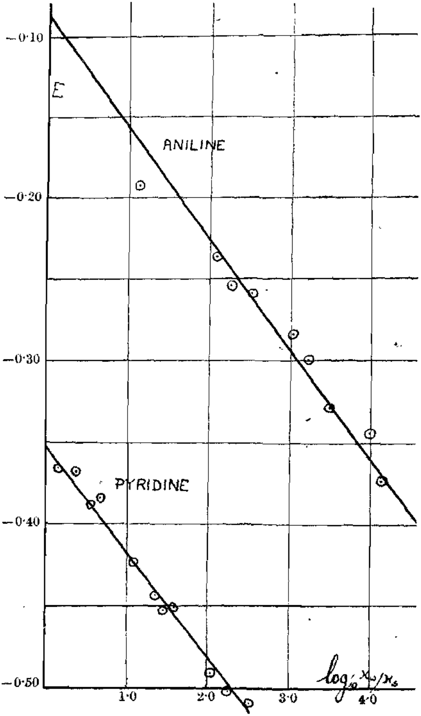
$$E = RT/F \,.\, \log_e P_w/rc_w - RT/F \,.\, \log_e P_s/rc_s + e$$
$$= RT/F \,.\, \log_e P_w c_s/P_s c_w + e.$$

In this expression, e is the liquid junction potential, which may be positive or negative, P_w and P_s are the electrolytic solution tensions of silver in water and in the organic solvent respectively, c_w and c_s are the ionic concentrations of the two solutions respectively, and r is a factor to convert concentration to pressure term

Further, on the classical view, $c_s/c_w = \kappa_s\Lambda_{\infty\,w}/\kappa_w\Lambda_{\infty\,s}$ so that

$$E = RT/F\,.\,\log_e P_w\Lambda_{\infty\,w}/P_s\Lambda_{\infty\,s} - RT/F\,.\,\log_e \kappa_w/\kappa_s + e \quad . \quad . \quad (1)$$

FIG. 1.



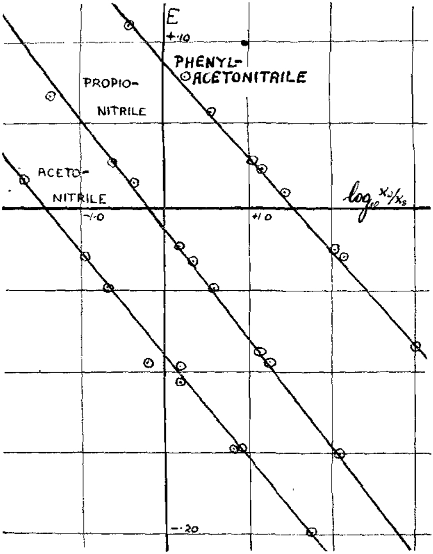
If this theoretical relationship is compared with the general empirical result of this investigation, *viz.*, $E = A \log_{10} \kappa_w/\kappa_s + B$, it appears that e must be expressible as the sum of two terms, one

a constant and the other involving $\log_{10} \kappa_w/\kappa_s$. Hence (1) assumes the form

$$E = b \log_{10} P_w\Lambda_{\infty w}/P_s\Lambda_{\infty s} - a \log_{10} \kappa_w/\kappa_s$$

and therefore $a = -A$, and $b \log_{10} P_w\Lambda_{\infty w}/P_s\Lambda_{\infty s} = B$. Since B has been determined in the present research, and the values of

FIG. 2.

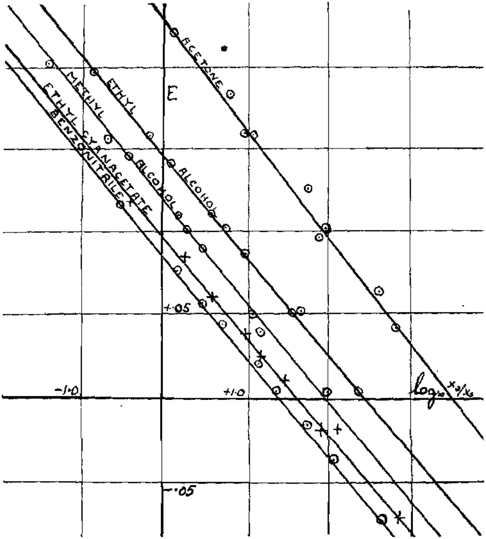


Λ_∞ in water and in the organic solvents can be obtained, the last equation would provide a means of calculating P_w/P_s if the value of b could be ascertained. This difficulty cannot be surmounted unless either e is known or some assumption is made regarding it. The latter course has been adopted, and it is assumed that when $E = 0$, $e = 0$ (compare Baur, *Z. physikal. Chem.*, 1923, **103**, 39; *Trans. Faraday Soc.*, 1924, **19**, 718). On this basis, from (1),

$\log_{10} P_w\Lambda_{\infty w}/P_s\Lambda_{\infty s} = \log_{10} \kappa_w/\kappa_s$, and $B = -A \log_{10} \kappa_w/\kappa_s = A \log_{10} P_w\Lambda_{\infty w}/P_s\Lambda_{\infty s}$.

The values of A and B are known for each solvent from t graphs (see Table II). The value of Λ_∞ for silver nitrate in water 25° is taken as 134 (Harkins, *J. Amer. Chem. Soc.*, 1911, **33**, 181 and the values of Λ_∞ for silver nitrate in the various orga

FIG. 3.



solvents have been obtained by taking as a starting point the val of Λ_∞ = 113 in methyl alcohol (Frazer and Hartley, *Proc. Ro Soc.*, 1925, **109**, *A*, 362) and calculating the others therefrom wi the help of the Walden rule: $\Lambda_\infty \times \eta$ = constant.* The figur employed for the viscosity (η) of the different solvents (taken eith from Walden, *op. cit.*, or from the Landolt–Börnstein Tabellen) a

* The values of Λ_∞ obtained by the above method are as comparable those given by different observers. Moreover, the data given in the literatu are scanty and not always trustworthy.

given in the second column of Table III, whilst the values of Λ_∞ derived, except for water and methyl alcohol, as stated above, are tabulated in the third column. The fourth column contains the values of P_w/P_s, and the fifth the normal potentials of silver calculated from the equation $\epsilon_n = 0{\cdot}7995 + 0{\cdot}058 \log_{10} P_w/P_s$, in which the normal potential of silver in water is taken as $+ 0{\cdot}7995$ (Lewis and Randall, "Thermodynamics," p. 414).

TABLE III.

Solvent.	η.	Λ_∞ for $AgNO_3$ at 25°.	P_w/P_s.	ϵ_n.
Pyridine	0·00894	71·4	$2{\cdot}05 \times 10^{-6}$	+0·470
Aniline	0·0374	17·1	$4{\cdot}90 \times 10^{-3}$	+0·666
Acetonitrile	0·00345	186·0	$5{\cdot}24 \times 10^{-2}$	+0·725
Propionitrile	0·00413	154·6	0·759	+0·799
Phenylacetonitrile	0·0193	33·1	8·64	+0·853
Ethyl cyanoacetate	0·0250	25·5	8·82	+0·854
Benzonitrile	0·0123	51·9	10·9	+0·860
Methyl alcohol	0·00565	113·0	81·1	+0·910
Ethyl alcohol	0·0111	57·5	150·0	+0·926
Acetone	0·00316	202·0	6043·0	+1·019

The values of P_w/P_s support the generally accepted view that the electrolytic solution tension of a metal varies with the solvent, but are in conflict with the attempted correlation of solution tension and dielectric constant (compare p. 270).

The suggestion has been made (Brodsky, *loc. cit.*) that the solution tension of a metal in different solvents should run parallel with the solubility of a given salt of the metal in these liquids, and with the object of testing this relationship the solubilities of silver nitrate in pyridine, aniline, propionitrile, phenylacetonitrile, and ethyl cyanoacetate have been roughly determined at room temperature (18°). Figures for the other solvents have been taken from Walden's book. In Table IV the various solvents are arranged in the order of diminishing solution tension, whilst the corresponding dielectric constants (*D.C.*) and solubilities (in g. per 100 g. of solvent) are set out in the second and third columns.

TABLE IV.

Solvent.	*D.C.*	Solubility.	Solvent.	*D.C.*	Solubility.
Pyridine	12·4	27	Ethyl cyanoacetate	27·7	35
Aniline	6·85	22	Benzonitrile	26·3	105
Acetonitrile	36·4	290	Methyl alcohol	35·4	3·7
Propionitrile	27·5	180	Ethyl alcohol	25·4	3·1
Water	81·7	270	Acetone	21	0·3
Phenylacetonitrile	15	75			

The results of the present investigation show that the solution tension of silver is definitely greater in pyridine, aniline, and aceto-

nitrile than in water, a relationship which is in conflict with the formulation of Baur and others (see p. 270). Altogether, there is an absence of any kind of order in the dielectric constants when the solvents are arranged in order of decreasing solution tensions as above, and there is also no obvious relation between the solubility of silver nitrate and the solution tension of the silver ion. It seems that the existence of specific attractive forces between the solvent molecules and the metal ion would account best for the observed effects, the high solution tension of silver in pyridine being due to this solvent's pronounced ammoniacal character.

Summary.

(1) The solution tensions and normal potentials of silver in various solvents at room temperature have been deduced by a new method.

(2) The results show that there is no relation at all between the solution tension (or normal potential) and the dielectric constant of the solvent.

(3) An explanation is sought in the action of specific attractive forces between the metal ion and the solvent molecule. Molecules containing groups of an ammoniacal or nitrile character are shown to have, in general, a greater affinity for the silver ion than those containing hydroxylic or ketonic groups.

In conclusion, the author desires to acknowledge his debt to Professor J. C. Philip, F.R.S., for the interest and valuable suggestions with which he has furthered this work.

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XL.—*The Effect of Catalysts on the Speed of Flame, Infra-red Emission, and Ionisation during the Combustion of Carbon Monoxide and Oxygen*

By W. E. GARNER and C. H. JOHNSON.

IN previous papers (Garner and Johnson, *Phil. Mag.*, 1927, **3**, 9 Johnson, *ibid.*, 1928, **5**, 301) it was shown that the loss of radia energy from explosions of carbon monoxide and oxygen, dried 1 2 hours over commercial phosphoric oxide, is nearly 10% of t total chemical energy set free during the explosion. With 1·9% water vapour present in the mixture, the fraction of the chemi energy emitted as radiation fell to one-quarter of the value for t

The explosions were carried out in metal tubes, 1 inch in internal diameter; under these experimental conditions, the hot products of explosion are rapidly chilled by the walls of the bomb, and the radiation emitted comes very largely from the burning gases. The amount of thermal emission from the hot products of explosion is thereby very much reduced, and the conditions are thus suitable for the detection of chemiluminescence if this be present in the radiant energy from the burning layers.

The temperature in the zone of combustion depends very largely on the velocity of chemical change, which is much more rapid in the moist than in the dry gases (Dixon, *Phil. Trans.*, 1884, **175**, *A*, 617). Thus the temperatures attained and the thermal energy emitted should be higher for the moist than for the dry gases. Experiment shows, however, that the emission of radiation is the greater for the dry gases. It must therefore be concluded that the difference between the emissions for moist and dry gases cannot be due to thermal emission but must be accounted for as chemiluminescence.

There is an intimate relationship between the speed of flame and the emission of radiation, which cannot be expressed in an exact manner on account of lack of knowledge of the mechanism by which the flame is propagated. It is clear, however, that the additional loss of 7·5% of the total energy of the explosion which occurs in the dry gases will reduce materially the velocity of the flame. It would appear, therefore, that one of the causes of the reduction in speed of flame in mixtures of carbon monoxide and oxygen which occurs on drying lies in the increased loss of energy as radiation.

Hydrogen and hydrogen-containing substances act similarly to water in promoting an increased speed of flame and in reducing the emission of radiant energy. The effects of ethyl nitrate, ethyl iodide, and hydrogen are similar to those of water. The magnitude of the changes produced on the addition of 1% is of the same order for all of these substances. The radiation emitted at 2·8 and 4·4 μ is diminished to practically the same extent as the total radiation.

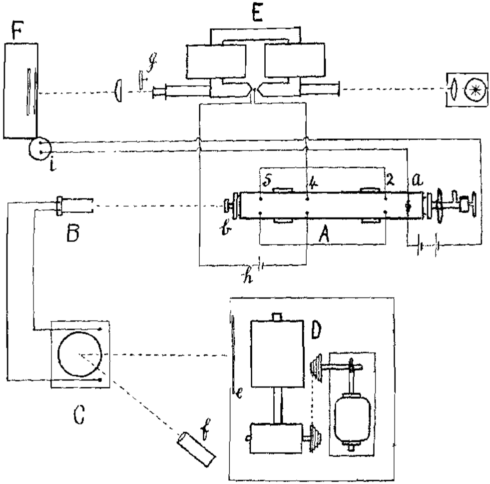
Other substances, such as carbon tetrachloride and nitrogen peroxide, have an opposite effect, decreasing the speed and increasing the emission of radiation. Their action is antagonistic to that of water, and it is highly probable that they reduce the concentration of this substance by interaction.

The extinction coefficients of the mixtures of carbon monoxide and oxygen, as measured in a column 10·7 cm. long, were not appreciably affected by the presence of the small quantities of the catalysts used. Thus the effects cannot be attributed to the absorption of radiation by the catalysts in front of the burning gases.

The changes in the emission of radiant energy occur in the region of the carbon dioxide maxima at 2·8 and 4·4 μ. We are thus dealing with an effect in which the molecules of carbon dioxide are concerned, and not those associated with the formation of some peculiarly active decomposition product of the catalysts employed.

These facts were established in a series of preliminary experiments and were confirmed later by more accurate measurements

Fig. 1.



with a new experimental arrangement by which the emission radiation, the ionisation, and the speed of flame could be measu simultaneously.

Experimental.

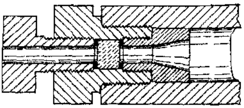
The disposition of the apparatus is shown in Fig. 1. The ga were fired in a cylindrical explosion vessel A of the same dimensi as that described previously. The ignition was brought about a by the fusion of very thin iron wire, 1·5 mm. long, stretc between the insulated terminals of a firing plug. A 12-volt batt was used as a source of current. The bomb carried in addition

pairs of insulated electrodes (only three are shown in the figure), which were placed between the firing plug and the fluorite window (*b*, Figs. 1 and 2). These were used in connexion with the measurement of speeds of flame.

In Fig. 3 a section is given showing the detailed construction of the electrodes. They carried stout platinum wires penetrating 0·4 cm. into the interior of the bomb, the tips of the wires of each pair being separated by 1·5 mm.

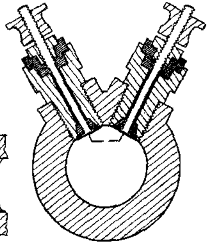
The bomb was clamped in a rigid iron framework in alinement with a sensitive, quick-acting, linear thermopile, B, mounted separately on a stand. The distance separating the fluorite window of the bomb and the thermopile was 34 cm., and in this position the

FIG. 2.



Section across fluorite window.

FIG. 3.



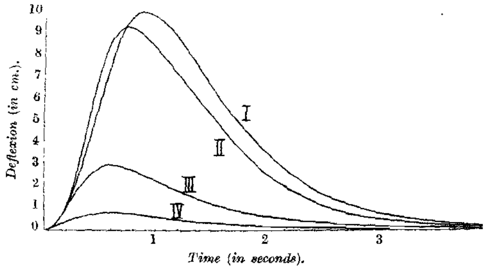
thermopile could not "see" the walls of the bomb. Both the bomb and the thermopile were fastened through their stands to the bench. The thermopile slit was maintained at 0·5 mm. throughout the experiments.

The thermopile was used in conjunction with a Downing galvanometer, C, which was enclosed in a shield of Mu-metal. The galvanometer was supported upon a slate slab resting on a 3-inch thickness of brown paper on the top of a brick column going down into the concrete foundations of the building, and this proved very effective in eliminating vibrational disturbances. A light mica damping vane attached to the suspension and a device for regulating the damping enabled the galvanometer to be critically damped when taking records. The sensitivity of the galvanometer was checked before every experiment by noting the deflexion produced when a small current from a standard cell passed through the coils of the instrument.

A photographic record was obtained of the galvanometer deflexion

by projecting a bright vertical line of light from a small filament lamp, *f*, upon the galvanometer mirror. This passed by reflexion to the adjustable horizontal slit of an improvised camera, D, placed about 40 cm. from the galvanometer and directly in front of it. Immediately behind the camera slit was a long cylindrical lens, *e*, which brought the line of light to a point focus upon a drum carrying Wellington and Ward "Negative Paper." Deflexions up to about 12 cm. could be recorded on the drum. A time marker, placed between the lamp and the galvanometer mirror (not shown in Fig. 1), was operated by the electrically driven tuning fork, which operated another time marker, *g*, used with the Einthoven galvanometer E. From the curves recorded on the revolving drum, the amounts of radiation falling on the thermopile could be calculated

FIG. 4.



The areas below these curves are proportional to the quantities radiation received. By comparing the areas obtained from expe ments on gaseous explosions with the area of a "control curve obtained by allowing a known amount of radiation to fall insta taneously upon the thermopile, the radiation received by t thermopile can be expressed in absolute units. The method obtaining the control curve has been described previously. Typi radiation records are shown in Fig. 4; the ordinates of the exp mental curves have been measured and re-plotted to the same ti axis, so that they are directly comparable. Curve I was obtai with standard dry mixture in the presence of carbon tetrachlori Curve II is a well-dried mixture; III is the record taken with gas; IV is the control curve.

Measurement of Flame Speeds.—A new method for the measu ment of flame speeds was devised which involved the use of

Einthoven galvanometer, E (Fig. 1), period $\frac{1}{350}$ second. The principle of the method is as follows: Each pair of the insulated electrodes in the bomb is connected in parallel with one another and in series with the string (movable part) of the galvanometer and a source of potential, *h*. Prior to explosion the gases in the bomb offer an infinite resistance and no current passes round the circuit; on exploding the gas mixture, the flame travels along the bomb, and as it passes each pair of electrodes it renders the gases conducting, thus causing a momentary deflexion of the fibre. These deflexions are recorded upon the falling plate of the Einthoven camera, F. The time of fall of the plate is automatically marked in twenty-fifths of a second, so that, the distances between the pairs of electrodes being known, direct measurements from the plates of the times between successive deflexions enable one to calculate mean flame speeds in the successive sections of the bomb. In practice, the method proved trustworthy only for the slowest flames, chiefly owing to the smallness of the bomb and the slow rate of fall of the plate. With a long bomb and a fast-moving drum in place of the falling-plate camera, this method would give highly accurate results, but in any arrangement a definite limit of usefulness is imposed by the period of the galvanometer, which may be comparable with the time taken by the explosion to traverse the distance between successive pairs of electrodes, in which case the fibre is set oscillating. The potential applied to the pairs of electrodes was either 2 or 4 volts according to the nature of the explosive mixture. In the very fast explosions, where considerable ionisation occurred, the galvanometer was shunted with a resistance equal to that of the fibre.

General.—It was found possible to co-ordinate the actions of both galvanometers, one recording radiation and the other speeds, so that simultaneous records were obtained of these properties in every explosion. By means of a simple device at *i*, it was arranged that the mechanism controlling the falling plate of the Einthoven camera automatically fired the bomb. In order to correlate completely the two photographic records, pieces of iron wire, similar to that used in firing the gas mixture, were affixed, one above the drum camera and another in front of the lens of the falling-plate camera, both connected in parallel with the firing plug. (These are not shown in the figure.) The wire above the drum was enclosed in a small black box with a slit so that the light emitted when the wire fused caused a sharp image of the slit to be registered upon the sensitised paper. By this means it was possible to determine if there was any appreciable lag between the moment of ignition of the gases in the bomb and the initial reception of heat by the thermopile. In

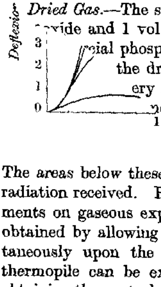
very few cases was a lag indicated, generally with dried gas mixture, and then only of the order of 0·01 sec. The fusing of the wire placed in front of the Einthoven camera removed its shadow from the plate.

Results.

Measurements of the total infra-red radiation and the speed of flame were made on a standard mixture of carbon monoxide and oxygen to which small quantities of catalysts had been added. The speeds were not determined with a high order of accuracy but are sufficiently exact to bring out the main points at issue. The data are collected in Tables I to VI. The emission of infra-red radiation decreases as the speed of flame increases, and *vice versa*.

In order to arrive at the values for the radiation received by the thermopile, the areas of the curves were measured and their equivalent calorific values calculated by comparison with the area of the control curve. These are expressed in calories, but any arbitrary scale would do equally well for the purposes of the present discussion. The speeds are the means of the velocity of propagatior between electrodes 2 and 4, and 4 and 5 (see Fig. 1). Usually th velocity was uniform in these two sections of the bomb.

Dried Gas.—The standard mixture consisted of 2 vols. of carbo ·xide and 1 vol. of oxygen, dried for two hours over 130 cm ·cial phosphoric anhydride before admission to the drie the drying was more complete than in the previou ery necessary to dry the bomb to the same exte ·ent. Only about one in every three mixture ·uld be fired by the fusion of iron wire, a iation between the individual results th



The areas below these curv owing, presumably, to the difficulty
radiation received. By com nb to the same extent each time. T
ments on gaseous explosions · in Table I.
obtained by allowing a know
taneously upon the thermop

TABLE I.

thermopile can be expressed ·ried gas.

obtaining the control curve has·

	2.	3.	4.	5.	Mea
·9	5·72	6·28	5·68	6·55	6·(
	108	79	130	89	100

radiation records are shown in
mental curves have been measu
axis, so that they are directly ·r *vapour*. The effect of addition
with standard dry mixture in ·peed is very marked. The radiat
Curve II is a well-dried mixtur·ue for the standard mixture by
gas; IV is the control curve. ·hilst the speed increases more t
Measurement of Flame Speed·ges of water vapour have a very g
ment of flame speeds was dev·ant energy emitted, as was show

removing two of the four tubes of phosphoric oxide, and by drying for 1 instead of 2 hours. The ratio of the emission from dry to that from wet gas fell from 3·5 : 1 to 2·5 : 1. In explosion 3 (Table II), the bomb was saturated with water vapour at 17·1°. This, therefore, corresponds to "wet gas" mixture. The water vapour in Nos. 1 and 2 was introduced into the evacuated bomb from water or ice maintained at a constant temperature.

TABLE II.

Dried gas + water.

Explosion No.	% Water.	Radiant energy (cal. × 10^6).	Speed (cm./sec.).
—	*0·00*	*6·00*	*100*
1	0·23	2·76	780
2	0·44	2·39	900
3	1·95	1·63	>1000

2. *Other positive catalysts.* A number of hydrogen-containing substances were added in order to compare their action with that of water. The vapours were in all cases introduced into the thoroughly dried bomb, and the explosive mixture was added subsequently, leaving time for thorough mixing. The vapours were strongly absorbed by the walls of the bomb, so that the percentages given in Tables III—VI are maximum values. Ethyl nitrate, ethyl iodide, ethyl bromide, and chloroform behave like water, increasing the speed and diminishing the radiant energy. They act as positive catalysts by virtue of the hydrogen they contain. In a number of experiments the speeds could not be read accurately from the records on account of overlapping of the deflexions. Nevertheless, even for the fastest explosions the order of magnitude of the velocity could be derived.

TABLE III.

Dried gas + hydrogen-containing substances.

Expl. No.	Catalyst.	% Added.	Radiant energy (cal. × 10^6).	Speed (cm./sec.).
—	—	*0·00*	*6·00*	*100*
1	$C_2H_5NO_3$	0·28	2·30	930
2	,,	0·46	2·20	>930
3	,,	0·89	1·56	2500 ?
1	C_2H_5I	0·18	2·16	>800
2	,,	0·32	1·67	1100
	C_2H_5Br	0·69	1·90	1100
	$CHCl_3$	0·47	2·30	560 ?

Negative Catalysts.—The effect of carbon tetrachloride upon the radiation intensity is not so marked as in the preliminary experi-

ments, doubtless owing to the more thorough drying of the standard mixture.

TABLE IV.

Dried gas + carbon tetrachloride.

Expl. No.	% Added.	Radiant energy (cal. × 10⁶).	Speed (cm./sec.).
—	0·00	6·00	100
1	0·35	6·34	79
2	0·72	6·60	44
3	1·05	6·84	63
4	1·42	6·47	55
5	1·14	6·49	81
6	1·01	6·97	57
Mean	—	6·62	63

TABLE V.

Dried gas + nitrogen peroxide.

Expl. No.	% Added.	Radiant energy (cal. × 10⁶).	Speed (cm./sec.).
—	0·00	6·00	100
1	1·09	5·10	110
2	1·63	4·67	133
3	?	4·78	169
4	From walls.	4·91	128
5	,, ,,	4·25	?

Nitrogen peroxide. Nitrogen peroxide behaves as a feebly positive catalyst in the mixture dried as above, but as a negative catalyst in an imperfectly dried mixture. In the earlier experiments, this vapour functioned as a negative catalyst.

TABLE VI.

Partially dried gas + nitrogen peroxide.

% Added.	Radiant energy (cal. × 10^{-6}).	Speed (cm./sec.).
0·0	3·94	375
<1·0	5·20	85 (approx.)

General Conclusions.—The relationship between the speed of propagation and the radiant energy has been shown to hold good within the error of experiment, for all cases examined. The emission intensity varies inversely with the speed of flame.

The behaviour of carbon tetrachloride and nitrogen peroxide is worthy of special consideration. Both substances can directly counter the action of water molecules, as has been demonstrated by addition of the vapours to partially dried gas mixture.

Carbon tetrachloride. Chemical interaction at high temperature between this vapour and the small amount of water present scarcely seems a sufficient explanation for the effect, since the product must obviously contain hydrogen and it is known that even hydrogen chloride (Dixon) and chloroform (Table III) behave as positive catalysts for the reaction. Nothing is known, however, regarding the relative efficiencies of the various hydrogen-containing catalysts.

It is scarcely conceivable that the energy absorbed from the system during the breakdown of the carbon tetrachloride and possibly, subsequent formation of oxides of chlorine, is of sufficient magnitude to reduce the flame temperature materially. Calculation

shows that if all the carbon tetrachloride is decomposed, the energy involved amounts to much less than 1% of the heat of combustion of the carbon monoxide. Even if this explanation were admissible in accounting for the slow rate of reaction, it would not explain the increased emission of infra-red radiation.

Nitrogen peroxide. The anomalous catalytic behaviour of this substance towards partly dried and thoroughly dried gas mixtures is readily understood if it is assumed that in the former case reaction occurs between the vapour and the water molecules, accompanied, maybe by adsorption of the resulting complex on the walls of the bomb. The net result is the substitution of a small amount of a feeble positive catalyst (nitrogen peroxide) for a smaller amount of an exceedingly powerful positive catalyst (water). This also explains why, in the preliminary experiments, nitrogen peroxide was found to be a less powerful negative catalyst than carbon tetrachloride.

Analysis of the Total-radiation Records.

The total-radiation curves give no direct information regarding the rates at which the energy is emitted from the bomb, since the galvanometer deflexion is determined by factors other than the emission of heat—notably by the inertia of the suspension and the various forces controlling its movements. A method of analysing galvanometer records (deflexion–time curves) has been developed by Hartree and Hill (*Proc. Roy. Soc.*, 1921, *A*, **99**, 172; *J. Sci. Inst.*, 1923, 267), by means of which the elimination of thermopile and galvanometer constants is possible. First, it is necessary to obtain a standard curve or " control curve " by recording the galvanometer deflexion when a known amount of energy is directed instantaneously upon the thermopile. It is assumed that when a certain quantity of heat falls suddenly on the thermopile, there is obtained a curve of definite shape with ordinates proportional to the amount of heat received. The underlying idea is the analysis of the experimental curve into a set of curves of the same shape as the control curve but of different magnitudes, their starting point as regards time being determined by trial. The effect is thus to divide what is in reality a continuous emission of heat from an explosion, into a succession of discrete impulses of energy, given out at definite small intervals of time. The closer the intervals are together, the more nearly does the derived rate of emission correspond to the actual rate.

The control curve is obtained by radiating to the thermopile a known amount of heat over a time short enough to be considered instantaneous in comparison with the duration of an explosion, the

thermopile and galvanometer being used under precisely the same conditions (as regards sensitivity, slit width, etc.) as when recording radiation from the explosions. The control curve is time-marked so that the ordinates (deflexions) can be measured every twenty-fifth of a second. This series of ordinates, then, corresponds to the reception by the thermopile of an arbitrary unit of heat; multiples and sub-multiples of these ordinates are tabulated, corresponding to multiples and sub-multiples of this arbitrary energy unit. This is the "Control Table." The explosion curve is measured up in the same way, and its ordinates are written in a horizontal column at the top of a large sheet of paper. From inspection of the first two or three of these it is seen that they agree more or less with the numbers in the control table corresponding to heat, say, x units at time 0; these numbers in the control table are then subtracted throughout from the tabulated ordinates of the experimental curve, and a note made, x units at time 0. The first two or three remainders are then seen to correspond to heat, say, y units at time 0·04 second (this being the interval chosen), and the numbers for y units in the control table are therefore shifted along to 0·04 second, and subtracted throughout, leaving a second series of remainders. The process is continued until the remainders become zero, or practically so.

The space required prohibits the reproduction of the operations by which the analysis is carried out; this was performed upon average curves obtained by measuring the ordinates of all the experimental curves and taking means at corresponding times after the instant of ignition.

TABLE VII.

Rates of emission of radiant energy.

Time from ignition (in $\frac{1}{25}$-sec. periods)	0	1	2	3	4	5	6	7
				Heat units.				
Wet gas	1·25	1·25	1·56	—				
Partially dried gas	1·25	1·5	2·0	2·25	1·9	1·9		
Dried gas	1·25	1·5	1·5	1·75	1·5	1·75	1·5	1·5
Dried gas + CCl_4	1·25	1·25	1·5	1·25	1·25	1·0	1·0	1·0

Time from ignition (in $\frac{1}{25}$-sec. periods)	8	9	10	11	12	13	14	15
				Heat units.				
Wet gas								
Partially dried gas								
Dried gas	1·25							
Dried gas + CCl_4	0·75	0·75	0·75	0·75	0·75	0·75	1·0	—

Each horizontal series in Table VII represents a succession of discrete impulses of heat given to the thermopile at intervals of 0·04 sec.; time 0 corresponds to the instant of ignition. The

thermopile receives practically the same quantity of radiant energy from each section of the bomb (see *Phil. Mag.*, 1928, **5**, 301), so that with a uniform flame movement an almost steady rate of emission would be recorded, provided that the bulk of the energy is received from the wave front and not from the hot products of combustion. The above table indicates that these conditions hold fairly well. Absorption by the cold gases diminishes the amount of radiation received from the initial stages of combustion, and retardation of the flame as it approaches the fluorite window reduces the quantity radiated per 0·04 sec. in the slower-moving flames.

Except for small residues, the radiation ceases abruptly at times dependent upon the nature of the catalyst present. These residues of heat, which are emitted some time after the steady radiation has ceased, probably have considerable theoretical interest and are therefore recorded in Table VIII.

TABLE VIII.

Heat residues.

	Dried gas $+ CCl_4$.		Dried gas.			Partially dried gas.	Wet gas.
Time from ignition (secs.)	1·1	2·7	0·8	0·9	1·1	1·4	—
Heat units	0·75	0·75	0·5	0·5	0·25	0·5	—
Total residue	1·5			1·25		0·5	—
% of total radiation ...	9·1			8·5		4·4	—

The duration of this residual radiation cannot be measured accurately without considerable refinements in the experimental technique (notably in the accuracy of time-marking the records) and without increasing enormously the labour of analysis. The time values tabulated above have therefore very little significance except as rough indications of the times over which the after-radiation was appreciable.

The residual radiation can hardly be thermal, since none is detected after explosions of wet gas mixture in which the highest temperatures are reached. If it is due to "after-burning," then considerable chemical combination must occur at low temperatures, which suggests the persistence of activated (or possibly ionised) molecules.

Evidence is submitted subsequently which points to a possible connexion between this residual radiation and the persistence of ions in the gases after explosion.

The Duration of Emission of Radiant Energy and the Duration of Flame.

It seemed of interest to attempt to correlate the duration of steady radiation with the duration of flame within the bomb.

The duration of radiation, exclusive of residues, can be compute directly from the above analyses. The duration of flame can b calculated from speed measurements—small inaccuracies are liabl to be introduced here owing to the somewhat unsatisfactory metho of recording the instant of ignition upon the plates. In three case in which dried gas mixture was used, it was possible to measur the speed between the moment of ignition and terminal 5, and th mean speed thus calculated was 93 cm./sec. Reference to Table shows the average speed for explosions in dried gas to be 100 cm./sec Calculation of the duration of flame was therefore made, taking th value 96 cm./sec. For carbon tetrachloride explosions, the mea speed between firing plug and T_5 was 67 cm./sec., and betwee T_2 and T_5 63 cm./sec. (see Table IV). A value 65 cm./sec. wa therefore taken in making the calculation. Owing to the metho by which the analyses of the total radiation curves were effecte it must be emphasised that the figures in both columns of Table I are derived from averaged data from corresponding records, and ar therefore comparable.

TABLE IX.

Description.	Duration of steady radiation (sec.).	Duration of flame (sec.).
Dried gas	0·34 ± 0·02	0·36 ± 0·02
Dried gas + CCl_4	0·54 ,,	0·54 ,,
Partially dried gas	0·22 ,,	0·16 ,,
Wet gas	0·10 ,,	0·03 ,,

The table shows that, within the limits of accuracy of the analysis the abrupt fall in the emission of radiation coincides with th extinction of flame in explosions of standard mixture with an without carbon tetrachloride. The bulk of the radiant energy therefore, has its origin in the wave front where chemical change i proceeding, and not in the hot products of reaction. This is als supported by the aforementioned fact that the energy is emitte at an approximately uniform rate as the flame travels along th bomb (see Table VII). Had emission occurred to any importan extent behind the wave, it would have been much less in the firs than in the last twenty-fifth of a second. The small diameter o the bomb is responsible for rapid cooling of the gases and ver probably for the sudden extinction of the radiant energy when th flame reaches the window.

When water is present the radiation outlasts the period o inflammation; in this case the flame temperature is higher, so tha a considerable proportion of radiant energy may be of therma origin.

Ionisation Phenomena accompanying Explosions of Carbon Monoxide and Oxygen. After-burning.

The speed records give comparative measurements of the maximum conductivity produced at the separate terminals and of its duration. It was not feasible to introduce the elaborations (guard-rings, etc.) necessary for a thoroughly trustworthy examination of ionisation, owing to the danger of screening off portions of the bomb from the thermopile and thus materially reducing the amount of radiant energy received upon it. Typical records are given in Figs. 5 and 7. The deflexions obtained are proportional to the electric current produced when the wave passes the platinum-point electrodes 2, 4, and 5.

The maximum deflexions obtained at electrode 2 for a number of explosive mixtures are recorded in the Table X under the heading of maximum conductivity, together with the speeds of flame and the persistence of ionisation at electrode 5.

The conductivity between platinum-point electrodes is dependent upon a large number of factors, *e.g.*, the rate of establishment of the ionisation equilibria, the nature of the elementary substances present, and the velocity of chemical change. It is not surprising, therefore, to find that the type of deflexions obtained for explosions in which various hydrogen-containing catalysts are present are similar to one another and different from that of the dried gases without catalyst. It is evident from Table X (*a*) that hydrogen-containing substances greatly increase the conductivity and decrease the duration of ionisation.

TABLE X.

Ionisation and speed of flame.

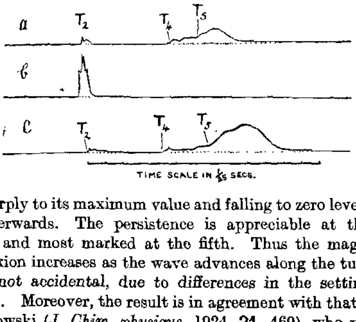
% Catalyst.	Speed of flame (cm./sec.).	Maximum conductivity (arbitrary units).	Persistence of ionisation at T_5 (sec.).
—	100	1·0	3·25 × 0·04
(*a*) Addition of hydrogen-containing substances.			
0·23 H_2O	780	8·5	0·8 × 0·04
0·44 ,,	900	17·0	0·6 ,,
1·95 ,,	>1000	30·0	0·4 ,,
0·28 $C_2H_5NO_2$	930	7·0	0·9 ,,
0·46 ,,	>930	11·0	0·7 ,,
0·89 ,,	2500	28·0	0·4 ,,
0·32 C_2H_5I	1100	>12·0	1·0 ,,
0·69 C_2H_5Br	1100	>10·0	0·9 ,,
0·47 $CHCl_3$	500 ?	12	1·6 ,,
(*b*) Addition of carbon tetrachloride and nitrogen peroxide.			
CCl_4	63	1·7	5·6 × 0·04
NO_2	140	2—8	2·5 ,,

Addition of Negative Catalysts.—Anomalous results are obtained with carbon tetrachloride; in spite of the fact that it reduces the speed, the conductivity is somewhat increased, and the persistence of ionisation lengthened. Nitrogen peroxide behaves normally, increasing both speed and conductivity and diminishing the persistence. The conductivity results in the presence of nitrogen peroxide are, however, erratic.

The Persistence of Ionisation.

A striking feature about explosions of dried standard mixture and of mixtures containing carbon tetrachloride is the persistence of ionisation for some time after the passage of flame across the electrodes. The persistence is not often evident at the first pair of electrodes (nearest the firing plug), the galvanometer deflexion

FIG. 5.



rising sharply to its maximum value and falling to zero level immediately afterwards. The persistence is appreciable at the fourth electrode and most marked at the fifth. Thus the magnitude of the deflexion increases as the wave advances along the tube. This effect is not accidental, due to differences in the setting of the electrodes. Moreover, the result is in agreement with that obtained by Malinowski (*J. Chim. physique*, 1924, **21**, 469), who previously observed the effect in slow-moving benzene–air mixtures. In Fig. 5 are reproduced some of the actual records in order to illustrate the various points at issue. Curve *a* shows a typical record obtained from a dried gas explosion, witb 4 volts across the terminals; the three breaks are clearly marked and the persistence of ionisation in the neighbourhood of T_4 and T_5 is very striking. Curve *b* was taken in the presence of ethyl nitrate with a *P.D.* of 2 volts and with the galvanometer shunted. Owing to the high speed of explosion, only the break corresponding with T_2 can be clearly distinguished. Curve *c* is a record obtained with carbon tetrachloride in the bomb, and a *P.D.* of 4 volts; the extraordinarily

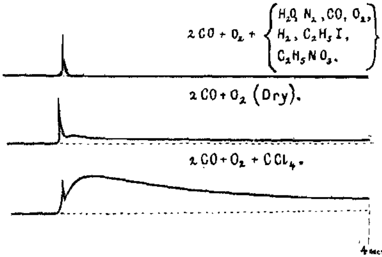
large deflexion, caused by an overlap of the effects at T_4 and T_5, and its long duration are obvious.

These results are in complete harmony with some unpublished experiments by Dr. S. W. Saunders, whose results are illustrated in Fig. 6, which is self-explanatory. In his work the electrode pair consisted of two platinum discs fitted with a guard ring, and the bomb was a spherical vessel of 2 litres capacity. The maximum deflexions are not directly comparable, since different voltages and galvanometer shunts were used in the three curves shown in Fig. 6.

Discussion.

The ionisation results show that in the presence of hydrogen-containing substances the conductivity of the gases falls from its

Fig. 6.

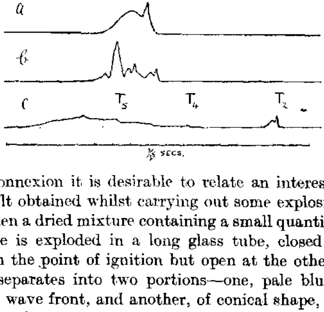


relatively high maximum value to zero within 0·02—0·03 sec. after the flame has reached an electrode. In explosions of dried gas mixture the ionisation at T_5 lasts for about 0·13 sec. after the passage of flame, and for 0·22 sec. in the presence of carbon tetrachloride. If this phenomenon were due primarily to "after-burning" (which Dixon and others claim to have found in dried mixtures of carbon monoxide and oxygen), it would surely have betrayed itself by appreciably prolonging the radiation of heat with respect to the duration of flame. The analyses of the radiation curves show, however, that the period of after-burning, if any, is too short to be detected with the experimental arrangement employed, and that the extinction of steady radiation practically coincides with the extinction of flame.

The long duration of ionisation can be interpreted on the assumption of an abnormally slow rate of recombination of the ions produced during combustion. It is natural to inquire whether this

retarded neutralisation is in any way connected with the emission of "residual" infra-red radiation, mentioned previously, which the analyses disclosed. The two effects certainly run parallel to one another. They also call to mind the recent results of Ellis and Wheeler (J., 1927, 310), in which it was discovered that, immediately following the wave front in mixtures of carbon monoxide and oxygen, an intense visible luminescence set in, originating in the neighbourhood of the point of ignition. This is attributed by the authors to "after-burning," but it is conceivable that the secondary emission of visible radiation is due to the recombination of ions produced during the passage of flame, or to the return of electrons in excited molecules of carbon dioxide to their normal orbits. The small amounts of residual infra-red radiation, detected in our experiments and emitted after the flame has reached the window, and the emission of visible radiation may be complementary phenomena.

Fig. 7.



In this connexion it is desirable to relate an interesting experimental result obtained whilst carrying out some explosions in glass tubes. When a dried mixture containing a small quantity of carbon tetrachloride is exploded in a long glass tube, closed at the end remote from the point of ignition but open at the other, the flame sometimes separates into two portions—one, pale blue in colour, forming the wave front, and another, of conical shape, emitting an intense yellow luminescence and separated by a few mm. from the first—the whole having a length of about 5 cm. When no separation occurs, the two zones are readily distinguished in the flame.

It is impossible to trace the shape of the ionisation records for the fast explosions, but close examination of the numerous cases where the speed is moderate or slow reveals a rather striking phenomenon which suggests an explanation of the above phenomenon.

Fig. 7 *a* represents the general configuration of a deflexion at a single electrode. There are two maxima; the first, which is sharp, undoubtedly corresponds to the passage of flame over the electrode; the second, which is usually less well-defined and smoother, is of

unknown origin. As an illustration, an actual record taken with a mixture containing a trace of water vapour is reproduced in Fig. 7 *b*, in which the double deflexions corresponding to T_2, T_4, and T_5 are clearly differentiated.

The form of some of the Einthoven records for explosions of dried gas mixture, and particularly in the presence of carbon tetrachloride or nitrogen peroxide, suggests the occurrence of simultaneous propagation of two waves within the bomb, travelling at approximately equal speeds. Fig. 7 *c* is an illustration of this type of record, in the presence of carbon tetrachloride; Figs. 5 (*a* and *c*) and 6 (Dr. Saunders) also illustrate it.

This effect may, however, be nothing more than a separation of the two maxima referred to above. Whatever the cause, there seems definite evidence for the existence of two "zones" of ionisation, which become more clearly differentiated the slower the combustion. Whether the flame actually divides into two portions within the bomb is a matter of conjecture; if such is the case, it is curious that the times for the duration of flame and radiation of heat are so nearly equal. The logical conclusion is that the infra-red emission from the second portion is very small.

The evidence for "after-burning" in explosions of carbon monoxide and oxygen rests chiefly upon the results of photographic examination. The interest attaching to the experiments described above is that a distinction is drawn between the combustion phase, with its attendant emission of infra-red energy, and another phase, the chief features of which are ionisation and an emission of visible radiation. The so-called "after-burning" may be nothing more than the registration of the latter upon a photographic plate.

Wheeler and Ellis (*loc. cit.*) have ascribed the after-glow to "after-burning," but it is conceivable, as already suggested, that it is merely a luminescence accompanying the neutralisation of ions.

It is impossible at present to do more than direct attention to the facts and to suggest an alternative explanation; further investigation must precede a detailed discussion of these curious phenomena.

Summary.

Measurements have been made of the rate of emission of radiation, the duration and magnitude of ionisation, and the speed of flame for carbon monoxide and oxygen mixtures to which a number of catalysts have been added.

Hydrogen-containing substances diminish the emission of infra-red radiation, and increase the speed of flame and the magnitude of ionisation in these explosions.

In an explosion of the dry gases, two maxima of ionisation are

observed to move past the electrodes as the flame traverses the explosion vessel. These simulate the passage of two successive waves. The second maximum is frequently much larger than the first, especially when carbon tetrachloride is present. The persistence of the ionisation associated with the second maximum increases as the wave passes along the bomb. At the last electrode it persists for 0·1—0·2 sec. These phenomena do not appear to be due to reaction between carbon monoxide and oxygen, since the infra-red radiation emitted after the flame has reached the window of the bomb is small. It may be an effect due to the absorption of ultra-violet radiation by the hot gases behind the flame, with the production of ions which are relatively stable in the absence of water. The recombination of these ions may be the cause of the emission of visible radiation observed by Ellis and Wheeler to occur after the passage of the flame.

These phenomena disappear in the presence of hydrogen, the addition of which increases the rate of attainment of thermal equilibrium both in and behind the burning layers.

The authors wish to express their indebtedness to Messrs. Brunner Mond & Co., whose grants for apparatus have made the above work possible, and to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant to one of them (C. H. J.).

THE WILLIAM RAMSAY LABORATORIES OF INORGANIC AND PHYSICAL CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [Received, December 8th, 1927.]

XLI.—*A Chemical Method for preparing Carbon Hydrosol.*

By EUGEN CHIRNOAGA.

IN the course of an investigation on the catalytic decomposition of aqueous solutions of sodium hypochlorite, it was found that charcoal acts very vigorously. The action is not, however, a purely catalytic one, for the charcoal is oxidised with the formation of carbon dioxide. It was noticed that when the charcoal was treated repeatedly with solutions of the hypochlorite, the liquid acquired a yellowish-brown colour and evidently contained a carbon (or possibly carbonaceous) sol. In most of the experiments described in this paper, a purified form of charcoal was employed, which had been boiled with concentrated hydrochloric and hydrofluoric acids and repeatedly washed with water until its ash content (mainly

silica) was reduced to 0·2—0·3%. The charcoal had also been heated to 900° in a high vacuum and had been used in experiments on the adsorption of oxygen gas, by which means any adsorbed hydrogen was removed.

0·3 G. of the charcoal was placed in a flask and 100 c.c. of distilled water were added; 5 c.c. of sodium hypochlorite solution (prepared from chlorine gas and alkali solution, and approximately $M/4$ with respect to NaClO) were poured into the flask and the mixture was rapidly stirred in a thermostat at 25°. Similar amounts of the hypochlorite solution were added at intervals of 2—3 hours. The concentration of the hypochlorite solution is immaterial, but in order to obtain a concentrated sol, a fairly large amount of hypochlorite is necessary. As the increasing concentration of sodium chloride is prejudicial to the stability of the sol, it is best to stop the operation from time to time and remove the sodium chloride by dialysis before adding more hypochlorite. It is also advisable to start with small amounts of charcoal and gradually work up the concentration of the sol. The colloidal solution thus obtained is now dialysed until it is as free as possible from extraneous electrolytes. In this condition, it reacts neutral to the usual reagents and is very stable (no deposition was observed after several months). It can be evaporated on the water-bath without undergoing any perceptible change, and if the operation be carefully conducted, the residue passes back into colloidal solution on the addition of water. The colour of the dilute solution is yellow by transmitted light, and that of the concentrated sol, viewed in a thin layer, varies from burgundy-red to dark brown. The colloid is not destroyed on being boiled with concentrated nitric acid. If a little of the sol be treated with a few c.c. of concentrated hypochlorite solution, the carbon particles are gradually completely oxidised and a clear colourless solution is obtained. The solid residue obtained by evaporating the dialysed sol at 100° loses about 20% of its weight on prolonged heating at 300°, and this loss is probably due mainly to the removal of adsorbed water.

Cataphoresis measurements showed that the sol particles are negatively charged (moving towards the positive electrode with a velocity of 70×10^{-6} cm./sec. under a gradient of 1 volt per cm.). It is probable that the negative charge is due to the adsorption of chlorine (and possibly hydroxyl) ions. This assumption is supported by the high precipitating power of the univalent silver ion (see following table).

Coagulation by Electrolytes.—The coagulating power of various electrolytes has been measured, and the results are summarised in the following table.

Coagulation of carbon sol by electrolytes.

Electrolyte.	Limiting value (millimols./litre).	Relative coagulating power.	Degree of precipitation.
$NaNO_3$	2500	0·4	Not complete.
$AgNO_3$	9·1	110	Complete.
LiCl	1180	0·84	Not complete.
NaCl	1000	1·0	,, ,,
KCl	552	1·8	,, ,,
$CaCl_2$	2·6	384	,, ,,
$SrCl_2$	1·6	625	,, ,,
$BaCl_2$	1·15	865	Complete.
$Ba(NO_3)_2$	1·3	770	,,
$AlCl_3$	0·86	1163	Not complete.
$Al(NO_3)_3$	1·1	909	Complete.
$Th(NO_3)_4$	0·6	1540	,,
NaOH	682	1·46	,,
$Ba(OH)_2$	4·5	222	,,

These results can only be regarded as rough approximations, as the minimal values were not always well defined. They confirm the cataphoresis experiments, and show that the sol contains particles stabilised by the adsorption of negative ions.

Size of Particles.—On the assumption that the carbon particles possess the density of graphite (2·16), an ultramicroscopic examination of a sol containing 0·325 g. of dry residue per litre gave 60 $\mu\mu$ for the average radius of the particles. Another sol containing 0·88 g. of dry residue per litre gave 68 $\mu\mu$ for the average radius. Some of the particles in these sols must be very small, for a double membrane of collodion and parchment paper did not prevent the diffusion of a certain amount of the sol. For this reason attempts to measure the osmotic pressure did not give constant and steady results. It may be remarked, however, that relatively high values for the maximum observable pressure were obtained. Thus, in the case of a sol containing 0·325 g. of dry residue per litre, the maximum osmotic pressure, observed at 25° after several changes of the outside water, was equal to 20 cm. of water.

Carbon Ink.—If a dialysed sol of carbon, prepared in the manner described in this paper, be evaporated on the water-bath, a brownish-black, thick liquid is obtained which can be used as an ink. The writing has a sepia colour and is resistant to washing and to the action of chemical agents. This fact may possess some technical value, as it was also found possible to prepare these stable carbon sols from unpurified commercial charcoal.

Theory of Formation of the Carbon Sol.—Although a chemical examination of the dry residue obtained from the sols described in this paper is reserved for a future communication, it is suggested that the particles consist essentially of carbon, and that the formation of the sol is due to the gradual breaking down or "etching" of

the surfaces of the particles of charcoal (caused by chemical oxidation to carbon dioxide) whereby particles possessing vigorous Brownian motion are produced, these being stabilised by the adsorption of chlorine (or hydroxyl) ions derived from the hypochlorite solution.

Summary.

1. A carbon hydrosol has been prepared from purified and from unpurified charcoal by the oxidising action of solutions of sodium hypochlorite.

2. The well-dialysed sol is very stable and can be evaporated at 100° *without irreversible coagulation.* It exhibits all the properties of a finely dispersed negative sol.

3. From these sols a good, brown, carbon ink can be obtained.

The author desires to express his thanks to Professor F. G. Donnan for his interest and help, and to Dr. McKie, of this laboratory, for kindly supplying the samples of purified charcoal.

THE SIR WILLIAM RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, January 5th*, 1928.]

XLII.—*The Electro-deposition of Indium with the Dropping-mercury Cathode.*

By SEISI TAKAGI.

NUMEROUS investigations with the dropping cathode have been carried out by J. Heyrovský and his collaborators (*Phil. Mag.*, 1923, **45**, 303; *Trans. Faraday Soc.*, 1924, **19**, 692; *Rec. trav. chim.*, 1925, **44**, 488—607). The method consists essentially in determining from the current-*E.M.F.* curves the cathode potential which corresponds to the deposition of metal (from a solution of a metallic salt) at the constantly renewed surface of the mercury cathode; in many cases this cathode potential is related to the metal-ion concentration in the simple reversible manner indicated by the classical Nernst logarithmic equation, and is thus, when reduced to normal concentration, characteristic of the particular ion. The method is described as being sensitive enough to detect many metals in a few c.c. of their aqueous solutions and at concentrations as low as $10^{-6}M$, and is obviously capable of many useful applications to qualitative and quantitative analysis, as indeed Heyrovský has already shown. The present investigation deals with the behaviour of acidified indium trichloride solutions when electrolysed with a dropping-mercury cathode, and with the

qualitative and quantitative determination of indium by this method in the presence of zinc and gallium.

EXPERIMENTAL.

Preparation of the Indium Solutions.—The indium was obtained from Messrs. Adam Hilger, Ltd., and had been subjected to a detailed spectrographic analysis. Its composition was given as: In 99·5, Zn 0·4, Na 0·04, Si *ca.* 0·01, Pb 0·005, Sn *ca.* 0·001%, with traces of Ca, Al, and Mg.

The solutions were prepared by dissolving the metal in pure redistilled hydrochloric acid with the aid of a platinised platinum foil, the acid being used in excess to prevent hydrolysis of the indium trichloride and also to improve the electrical conductivity of the solution. The indium concentration was calculated from the known mass of metal dissolved.

Method and Apparatus.—The procedure described by Heyrovský and Shikata (*Rec. trav. chim.*, 1925, **44**, 496) was followed very closely. The current–potential curves were obtained by the photographic method, and by the use of a "polarograph" very kindly presented to this laboratory by Professor Heyrovský. The sensitivity of the galvanometer used was carefully determined, and kept constant throughout the measurements at $1{\cdot}5 \times 10^{-8}$ amp. per mm. scale deflexion, the scale being 1 m. distant from the mirror. In order to determine the metal deposition point, *i.e.*, the potential corresponding to the "turning point" of the current–voltage curve, the 45°-tangent was always used.

In the following tables, c denotes the concentration of the indium trichloride in mols. per litre, E the observed decomposition *E.M.F.*, π_0 the observed potential difference of the bottom mercury layer (anode) from a standard normal calomel electrode, π' the deposition potential of indium from the given solution ($\pi_0 - E = \pi'$) and π_N the normal deposition potential of indium, *i.e.*, the calculated potential at which the ions from a solution containing 1 g.-mol. of indium ion per litre would be deposited. Assuming reversible deposition and the validity of the Nernst equation, the calculation depends on the use of the equation

$$\pi_N - \pi' = RT/nF \,.\, \log C_N/C, \text{ where } C_N = 1 \text{ and } n = 3.$$

All the measurements described in this paper were carried out at room temperature (approx. 17°).

Indium Trichloride in 0·1M-Hydrochloric Acid.—The results of the electro-deposition in $0{\cdot}1M$-hydrochloric acid, but with various indium concentrations, are in Table I. For measuring the anode potentials, connexion with the normal calomel electrode was made

by means of a saturated solution of potassium chloride. It was not necessary to use the Bjerrum extrapolation method, since the liquid junction potentials were small (1 millivolt or less). All potentials are given in volts.

TABLE I.

$c \times 10^5$.	E.	π_0.	π'.	π_N.
1140	0·5814	+0·0466	−0·5348	−0·498
1140	0·5862	+0·0466	−0·5396	−0·503
114	0·6056	+0·0494	−0·5562	−0·500
114	0·6080	+0·0496	−0·5588	−0·503
11·4	0·6261	+0·0480	−0·5781	−0·503
1·14	0·6397	+0·0476	−0·5921	−0·496
1310	0·5786	+0·0434	−0·5352	−0·499
131	0·5974	+0·0484	−0·5490	−0·494
13·1	0·6219	+0·0468	−0·5751	−0·501
13·1	0·6224	+0·0474	−0·5750	−0·501
1·31	0·6386	+0·0472	−0·5914	−0·499
1150	0·5856	+0·0484	−0·5372	−0·500
115	0·6055	+0·0488	−0·5567	−0·501
115	0·6035	+0·0474	−0·5561	−0·500
11·5	0·6176	+0·0486	−0·5690	−0·494
10·5	0·6230	+0·0454	−0·5776	−0·502
				Mean −0·500

Table I shows that π_N, the calculated normal deposition potential of indium ions, remains sensibly constant, although c varies from $1{\cdot}14 \times 10^{-2}$ to $1{\cdot}31 \times 10^{-5}$. The mean value is −0·500 volt, reckoned from the normal calomel zero. These results agree very well with similar results obtained by Heyrovský in the case of many other metal kations. It was found in the present case that the turning point in the current–voltage curve almost disappeared when the concentration of indium trichloride fell to $10^{-6}M$.

Influence of Hydrochloric Acid Concentration.—The results given in Table II show that when in a dilute solution of indium trichloride the concentration of hydrochloric acid is decreased below $0{\cdot}1M$, the calculated value of π_N becomes less negative, and the turning point in the curve becomes indistinct and finally disappears. The effect of adding potassium chloride to the weakly acid solutions is to restore the turning point, although with diminishing concentration of potassium chloride the calculated value of π_N becomes increasingly more positive. The effect of diminishing the hydrochloric acid concentration cannot be attributed to hydrolysis of the indium salt, as this should make the deposition potential more, and not less, negative.

It appears from these results that both potassium chloride and hydrochloric acid, since they make the potential more negative, diminish the activity of the indium ions. The effect of higher concentrations of hydrochloric acid is shown in Table III. In

TABLE II.

Constant concentration of $InCl_3$ = $1{\cdot}15 \times 10^{-4}$ M.

Solution.	E.	π_0.	π'.	π_N.
0·01 M-HCl	0·6521	+0·096	−0·556	−0·481
0·004M-HCl		Turning point indistinct.		
0·001M-HCl		No turning point observable.		
0·1 M-KCl, 0·001M-HCl	0·6128	+0·0488	−0·564	−0·489
0·01 M-KCl, 0·001M-HCl	0·6483	+0·098	−0·550	−0·475
0·05 M-KCl, 0·001M-HCl	0·6445	+0·116	−0·529	−0·454
0·001M-KCl, 0·001M-HCl		No turning point observable.		

these strongly acid solutions the liquid junction potential became of more importance. The results from which the calculated values of π_N are placed in col. a were obtained when a saturated potassium chloride solution was used in measuring the anode potential, whilst those carried into col. b were obtained by using saturated and half-saturated solutions and applying the Bjerrum extrapolation method.

TABLE III.

					π_N.	
$c \times 10^5$.	HCl, N.	E.	π_0.	π'.	a.	b.
105	0·3	0·5903	+0·0218	−0·5685	−0·512	—
			+0·0256	−0·5647	—	−0·508
11·5	0·4	0·5958	+0·0064	−0·5894	−0·515	—
			+0·0194	−0·5146	—	−0·502
11·5	0·5	0·6013	−0·0010	−0·6023	−0·528	—
1050	1	0·5509	−0·0288	−0·5797	−0·542	—
			−0·0192	−0·5701	—	−0·533
105	1	0·5684	−0·0290	−0·5974	−0·541	—
			−0·0208	−0·5892	—	−0·533
10·5	1	0·5846	−0·0370	−0·6216	−0·546	—
			−0·0330	−0·6176	—	−0·542
1·05	1	0·6068	−0·0394	−0·6462	−0·552	—
			−0·0338	−0·6406	—	−0·546
105	3	0·5193	−0·0954	−0·6147	−0·558	—
			−0·0758	−0·5951	—	−0·539
10·5	3	0·5385	−0·1060	−0·6445	−0·569	—
			−0·0904	−0·6289	—	−0·553
1·05	3	0·5594	−0·1028	−0·6622	−0·569	—
			−0·0852	−0·6446	—	−0·550

It will be seen from Table III that the effect of increasing the hydrochloric acid concentration is to make the value of the normal deposition potential more negative, *i.e.*, to decrease the activity of the indium ions. This is in agreement with the results obtained by diminishing the hydrochloric acid concentration (Table II). It is possible that the addition of hydrochloric acid (or of potassium chloride) to the indium trichloride solution tends to produce anionic complexes containing indium, and thus to reduce the concentration of the simple indium kations.

The Influence of Sulphate Ions.—Some experiments were made in the presence of zinc sulphate, in order to test the applicability of the present method to the detection of indium in metallic zinc. These results are shown in Table IV. It is noteworthy that in the presence of 0·045M-zinc sulphate and 0·01M-hydrochloric acid, the turning point entirely disappears from the polarisation curve of a $1{\cdot}31 \times 10^{-4}M$-indium chloride solution, but reappears when the hydrochloric acid concentration is increased to 0·1M. In the latter case the normal deposition potential agrees well with that found in a solution containing only 0·1M-hydrochloric acid (in addition to the indium chloride). It will also be observed from the table that potassium sulphate acts similarly to zinc sulphate. The disturbing effect is therefore due to the sulphate ion, which, in the presence of an insufficient concentration of hydrogen ions, appears to remove indium ions, probably in the form of a basic salt. In the $1{\cdot}31 \times 10^{-3}$ M-solution of indium chloride, however, the turning point was obtained even in the presence of 0·045M-zinc sulphate and 0·01M-hydrochloric acid, and the corresponding normal deposition potential agreed well with that of a solution of the same composition in the absence of zinc sulphate.

TABLE IV.

$\times 10^5$.	Solution.	E.	π_0.	π'.	π_N.
131	0·045M-$ZnSO_4$, 0·01 M-HCl	0·6377	+0·0986	−0·539	−0·484
13·1	0·05 M-$ZnSO_4$, 0·001M-HCl	*No turning point for indium.*			
13·1	0·045M-$ZnSO_4$, 0·01 M-HCl	No turning point for indium.			
13·1	0·045M-$ZnSO_4$, 0·1 M-HCl	0·6278	+0·0524	−0·575	−0·501
1·31	0·045M-$ZnSO_4$, 0·1 M-HCl	0·6437	+0·0532	−0·590	−0·497
11·5	0·05 M-K_2SO_4, 0·001M-HCl	*No turning point for indium.*			
11·5	0·045M-K_2SO_4, 0·01 M-HCl	No turning point for indium.			
11·5	0·045M-K_2SO_4, 0·1 M-HCl	0·6274	+0·0534	−0·574	−0·500

Estimation of Indium in Metallic Gallium.—The sample of gallium was obtained from Messrs. Adam Hilger, Ltd. From the results of chemical and spectrographic analysis it was reported to contain 0·8% of indium. 0·1227 G. of this metallic gallium was dissolved in hydrochloric acid so as to yield 10 c.c. of a solution of the chloride in 0·1M-hydrochloric acid. When this solution was electrolysed with the dropping-mercury cathode, the turning points corresponding to the indium ion and the hydrogen ion were obtained on the current–voltage curves. Since the deposition potential of gallium

is near to that of hydrogen, but more negative, no turning point due to gallium ion is observable in the acid solution. For the turning point due to the indium ion the results were as follows: $E = 0{\cdot}6167$ volt, $\pi_0 = +0{\cdot}0402$ volt, $\pi' = -0{\cdot}5765$ volt. From the equation given on p. 302, by substitution of $\pi_N = -0{\cdot}500$ and $C_N = 1$, the molar concentration of indium in the solution was found to be $0{\cdot}00094$. Hence the indium content of the gallium metal was 0·88%.

Summary.

1. The electro-deposition of indium at the dropping-mercury cathode from solutions of the trichloride in $0{\cdot}1M$-hydrochloric acid was found to proceed reversibly in conformity with the Nernst logarithmic equation.

2. The normal deposition potential of the indium ion in the above solution was found to be −0·500 volt, with reference to the normal calomel electrode.

3. The normal deposition potential was found to depend on the concentration of the hydrochloric acid, being more negative the higher the concentration.

4. A remarkable effect on the deposition potential due to sulphate ion was observed and investigated.

5. The present method can be applied to the detection and estimation of indium in metallic zinc and gallium. For this purpose, the metals should be dissolved in hydrochloric acid and the free acid concentration should be $0{\cdot}1M$. The minimum concentration of indium chloride which can be detected and estimated in this manner is 10^{-5} mol. per litre.

6. The deposition potential of gallium cannot be determined in acid solutions.

This investigation was carried out while the author was a Ramsay Memorial Scholar. The author desires to express his thanks to Professor F. G. Donnan for kind advice and assistance.

THE SIR WILLIAM RAMSAY LABORATORIES OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, January 5th,* 1928.]

XLIII.—*Studies of Valency. Part VIII. Extinction Coefficients and Molecular Conductivities of Vernon's Isomeric α- and β-Dimethyltelluronium Salts. The Molecular Structure of Quadrivalent Tellurium Compounds.*

By Thomas Martin Lowry, (Mrs.) Rose R. Goldstein, and Frank Lathe Gilbert.

Few substances possess a greater interest from the stereochemical point of view than the isomeric tellurium compounds prepared by Vernon in 1920 (J., 1920, **117**, 86, 889; 1921, **119**, 105, 687). The initial product, α-dimethyltelluronium di-iodide, $TeMe_2I_2$, prepared by the direct action of methyl iodide on tellurium (Demarçay, *Bull. Soc. chim.*, 1883, **40**, 99) is a dark-red solid, the salt-like character of which was demonstrated by Vernon, who converted it by the action of silver oxide into an "α-base," to which he assigned the formula $TeMe_2(OH)_2$. When the solution was evaporated to dryness, this α-base was converted into an anhydrous "β-base," $TeMe_2O$, which gave a series of isomeric β-salts, such as the β-di-iodide, when acted on by acids. No process was discovered by which the β-base or its salts could be reconverted directly into the α-compounds, but both bases gave the same dimethyltelluride on reduction, and on reoxidation a mixture of both bases was produced, although only the α-dihalide was formed when the telluride combined with a halogen. These isomeric bases behaved differently towards silver nitrate, ferrous and ferric chlorides, platinic chloride and picric acid; moreover, whereas the α-di-iodide gave oxy-iodide when treated with potassium carbonate, the β-di-iodide gave rise to trimethyltelluronium iodide, $TeMe_3I$, as the result of a wandering of a methyl group, which may be compared with the pinacol–pinacolin transformation. Since, however, their general physical and chemical properties resembled one another somewhat closely, Vernon concluded that the two series of compounds were stereoisomerides; and, since the α-base was converted into the anhydride of the β-base by dehydration, he identified the α-salts as the *trans*- and the β-salts as the *cis*-form of a quadrivalent complex with a planar or square configuration.

With the possible exception of the β-base, these tellurium compounds do not possess any marked odour; but they have the objectionable property of liberating dimethyltelluride by a slow progressive reduction, the effects of which may persist for long periods after contact with the original materials. The conditions which Vernon

endured from this cause were indeed so intolerable that no further work on these compounds was attempted after the publication of his last paper in 1921, and it is only the fact that Vernon's own specimens were still in existence that led us to undertake the much less odious task of measuring their absorption spectra and molecular conductivities, without attempting to make any new material. At a later stage, when we had used up most of Vernon's specimens, we were fortunate in being able to secure from Dr. Alexander Scott an additional 20 grams of the α-di-iodide, and from this material a complete series of new specimens of the α- and β-salts was prepared.

The identity and purity of Vernon's specimens, which had been enclosed in sealed tubes and labelled, were guaranteed by their colour and beautiful crystalline character, but were also checked by melting-point determinations, which agreed precisely with Vernon's values. Only the β-di-iodide, which showed signs of decomposition, was recrystallised before being used. The purity of these specimens was also checked by comparison with fresh preparations from Dr. Scott's di-iodide, the only point of contrast being that the brilliant scarlet colour of Vernon's crystals of the α-di-iodide was not equalled in any other specimen. The β-dichloride, which Vernon described as "tinged" (but of which there was no specimen in his collection), was obtained quite free from colour, although with a rather lower melting point.

Absorption Spectra.

The striking difference in colour of the α- and β-dihalides shows that the isomerism of the α- and β-compounds must include some factor which is not expressed completely by merely putting two halogen atoms and two alkyl radicals at adjacent or at opposite corners of a square. Vernon himself (J., 1920, **117**, 86) showed that the β-compounds are more absorptive than the α-compounds in the ultra-violet as well as in the visible region of the spectrum; but it is difficult to assign any definite value to his transmission limits, in view of the fact that he did not detect the selective absorption which is the most striking characteristic of four out of six of these absorption spectra. The extinction coefficients of all the relevant compounds in Vernon's collection were therefore measured, but excluding in the first instance the β-dichloride, of which no specimen had been preserved.

These compounds were examined in *M*/100 to *M*/10,000-solutions in absolute alcohol, by methods which have already been described (J., 1924, **125**, 1921). When, however, the measurements of molecular conductivity had revealed the extreme sensitiveness of the dihalides to hydrolysis, even in the cold, the precaution was

taken of plotting a fresh series of curves for a complete set of new samples prepared from Dr. Scott's iodide, but using as solvent a sample of alcohol which had been purified by distillation in an all-glass apparatus from freshly burnt lime (three times) and from a mercury–aluminium couple (twice), and was shown by density determinations to contain less than 0·1% of water. Slightly higher values were then obtained for the molecular extinction coefficients of some of the solutions, but without change in the form or character of the curves. On the other hand, when an alcoholic solution of the α-di-iodide was diluted with four times its volume of water, the maximum at $\lambda = 3570$, $\log \varepsilon = 3{\cdot}7$, was reduced to a mere step-out at $\log \varepsilon = 2{\cdot}4$, the absorptive power of the solution being reduced about 20-fold and the highly selective character of the absorption being largely destroyed. *It is therefore possible that Vernon's failure to detect any selective absorption may have been due in part to a hydrolysis, which we should not have suspected if we had not* measured the conductivities as well as the absorption spectra of the salts.

TABLE I.

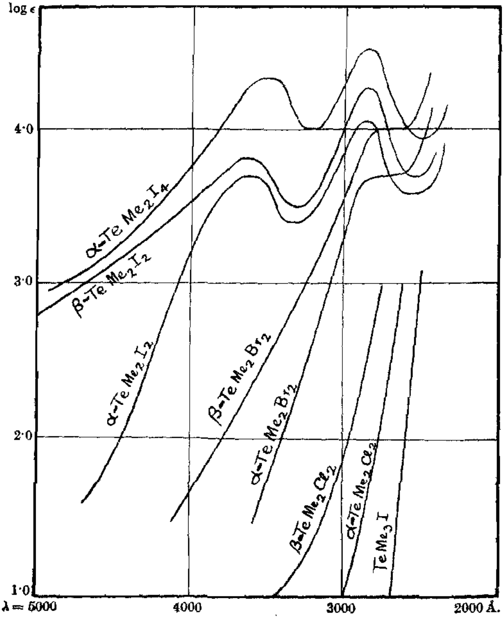
Extinction Coefficients of Quadrivalent Tellurium Compounds.

	Log ε =	1·0	2·0	3·0
$TeMe_3I$	λ =	2700	2600	2500
α-$TeMe_2Cl_2$	λ =	3000	2800	2600
β-$TeMe_2Cl_2$	λ =	3400	2900	2750
α-$TeMe_2Br_2$	Step out at λ = 2800 to 2600, log ε = 3·7			
β-$TeMe_2Br_2$	,, ,, λ = 2850 to 2650, log ε = 4·0			
α-$TeMe_2I_2$	Maxima at λ = 3570, log ε = 3·7; λ = 2840, log ε = 4·05			
β-$TeMe_2I_2$	,, λ = 3660, log ε = 3·8; λ = 2900, log ε = 4·25			
α-$TeMe_2I_4$	,, λ = 3610, log ε = 4·3; λ = 2900, log ε = 4·5			
KI_3	,, λ = 3550, log ε = 3·9; λ = 2900, log ε = 3·95			
CHI_3	,, λ = 3450, log ε = 3·4; λ = 2940, log ε = 3·5			

The new absorption curves are plotted in Fig. 1, and some of the more important extinction coefficients are set out in Table I. These observations show that, in spite of the marked differences in colour and in absorptive power to which reference has already been made, there is a fundamental similarity of *type* in the absorption spectra of the isomeric α- and β-compounds. For instance, the α- and β-dichlorides resemble trimethyltelluronium iodide in exhibiting only a general absorption of moderate intensity. The dibromides, however, both exhibit a well-marked "step-out," which is not shown by the dichlorides; thus, the molecular extinction coefficient of the α-dibromide remains almost constant at $\log \varepsilon = 3{\cdot}7$ over a range of 200 Å. from 2600 to 2800 Å. and, in the same way, the extinction coefficient of the β-compound remains almost constant at $\log \varepsilon = 4{\cdot}0$ over a similar range of wave-lengths. The most interesting compounds of the group are, however, the α- and β-di-

iodides, both of which give the characteristic twin maxima which we have already recorded in the absorption spectra of iodoform and of potassium tri-iodide (J., 1926, 622). This result is in marked contrast with the behaviour of methylene di-iodide, CH_2I_2, which

FIG. 1.



Molecular extinction coefficients of quadrivalent tellurium compounds.

shows only a single maximum; it therefore gives additional force to Vernon's contention that "the relationship between the four tellurium valencies must be different from that generally assumed to exist between the carbon valencies in such a compound as methylene iodide."

The α-tetraiodide, $TeMe_2I_4$, also gives two maxima, which agree fairly well in wave-length and intensity with those predicted for a mixture of one molecule of the α-di-iodide with one equivalent of the tri-iodide ion, the values for the latter being deduced from unpublished data for alcoholic solutions of the crystalline periodide, $C_6H_4Br\cdot\overset{+}{N}Me_3\overset{-}{I_3}$. The tetraiodide can therefore be formulated in the usual way as the tri-iodide of a univalent kation, $[\overset{+}{Te}Me_2I]\overset{-}{I_3}$, in harmony with Vernon's conclusion that, since the α-di-iodide can be reproduced unchanged by removing a molecule of iodine from the tetraiodide, the latter compound does not contain sexavalent tellurium. It is noteworthy, however, that, whereas one atom of iodine in the α-di-iodide can be converted into a periodide, the second atom of iodine does not yield a tri-iodide radical, even when acted on by an excess of iodine, and that the β-di-iodide does not yield even a tetraiodide under similar conditions.

Molecular Conductivities.

The molecular conductivities of these compounds were determined in order to ascertain whether the dihalides behave as binary or as ternary electrolytes,* since it was expected that, if they were binary electrolytes, the limiting conductivities would be of the same order as in the case of tetramethylammonium chloride, which gives $\Lambda_{\infty}^{25^\circ} = 46\cdot3 + 76\cdot55 = 122\cdot8$,† whereas if they were ternary electrolytes, the limiting conductivities might be nearly twice as great, since the hydrochloride of ethylenediamine,

$$\overset{-}{Cl}[\overset{+}{N}H_3\cdot CH_2\cdot CH_2\cdot\overset{+}{N}H_3]\overset{-}{Cl},$$

gives $\Lambda_{\infty}^{25^\circ} = 80\cdot9 + 2 \times 76\cdot55 = 234\cdot0$.

For these conductivity measurements a calibrated wire-bridge was used. Most of the measurements were made with conductivity cells which had been used by Bousfield and Lowry (Fig. 8, *Phil. Trans.*, 1905, *A*, **204**, 298) when determining the conductivity of standard solutions of sodium hydroxide. Duplicate determinations in two different cells gave concordant results; but, since the dilutions were made by the ordinary volumetric and not by gravimetric methods, these results are not to be regarded as standard data. Only integral values have therefore been given for the molecular conductivities of the solutions. The conductivity water was prepared in a Bousfield still and had a specific conductivity of 1 to 2 gemmhos.

* Compare Schilow's proof (*Z. anorg. Chem.*, 1924, **133**, 59) that mercurous nitrate is a ternary and not a binary electrolyte.

† There is very little difference between the three halogen ions, since Cl = 76·55, Br = 78·44, I = 77·2 at 25°.

The chief difficulty of the conductivity measurements arose from the sparing solubility of the salts in water. Vernon records that "on prolonged boiling" the α-di-iodide gives "an orange-red solution" which, on cooling, redeposits the iodide, leaving a perfectly colourless liquid, but that a "curious state of equilibrium" between the α-base and hydriodic acid results when a boiling saturated solution of the iodide is poured into a large excess of cold water. Under these conditions, a "fine yellow precipitate is formed" which quickly disappears, giving rise to a colourless solution, from which the iodide is at once precipitated on the addition of hydriodic acid. Vernon attributed these complex changes to hydrolysis of the iodide according to the equation $TeMe_2I_2 + 2H_2O \rightleftharpoons TeMe_2(OH)_2 + 2HI$; but the complexity of the phenomena suggested that this rather drastic treatment would not be likely to provide suitable conditions for a quantitative study of the conductivity of the undecomposed salts. We therefore chose, as a lesser evil, to dissolve the salts in the minimum amount of alcohol, and to drown the alcoholic solutions in cold conductivity-water, with the idea that the presence of a small proportion of alcohol would not alter the conductivities to such an extent as to prevent us from recognising the *type* of electrolyte with which we were dealing. Moreover, although the changes produced by heating the salts with water were obscure, there were sufficient data already available to show that the effect of alcohol on the *conductivity* of an aqueous electrolyte is about twice as great as its concentration; and in the same way, measurements of the vapour pressure of aqueous alcohol show that the effect of alcohol on the *activity* of the water is rather less than half as great as its concentration. The total effect produced by the presence of 2% of alcohol in the solution would therefore be to reduce the molecular conductivity of the salt by about 5%; moreover, since the proportion of alcohol was halved at each successive dilution, the conductivities of the weaker solutions would approximate more and more closely to those of solutions in pure water.

After most of Vernon's material had been used, a sufficient quantity of his α-di-iodide was left for an experiment on the "curious equilibrium" which is produced when the salt is hydrolysed by boiling water. A small quantity of the α-di-iodide was heated with water until it dissolved, and then poured into cold water; after the yellow precipitate had redissolved, the conductivity of the hydrolysed solution was measured. The values recorded agreed closely with those that had been obtained by diluting cold alcoholic solutions with a large excess of cold conductivity water, when the

which each solution contained. Thus, for the α-di-iodide, the following values were obtained :

	v	512 litres.	1024 litres.	2048 litres.	4096 litres.
Without alcohol	$\Lambda^{25°}$ =	*501(0)*	*509(0)*	*513(0)*	*517(0)*
,, ,,	......	509(0)	511(0)	513(0)	515(0)
With alcohol (corr.)		506(4)	515(2)	517(1)	515(0·5)
,, ,, ,,		502(2·5)	510(1·25)	513(0·6)	516(0·3)
Mean		505	510	514	516

The percentage of alcohol in each solution is shown by the figures in brackets. The corresponding figures for the α-tetraiodide are: with alcohol (corr.) 482(4), 489(2), 494(1), 495(0·5).

These experiments showed that the hydrolysis of the di-iodide gives rise to the same final equilibrium, whether the solution is prepared by dilution with water from an alcoholic solution of the unhydrolysed salt, or by cooling a hot aqueous solution, in which hydrolysis may have proceeded far beyond the normal limits of hydrolysis at lower temperatures. This discovery opened the way for a new series of confirmatory experiments, as soon as additional material became available. Aqueous solutions of the α- and β-*bases* were therefore prepared from Dr. Scott's specimen of the di-iodide, by the methods described by Vernon. A complete series of six *normal* salts was then made by adding the halogen acids to the bases, and recrystallising the precipitated salt from alcohol. Finally, aqueous solutions of the six corresponding *hydroxy*-salts were prepared by mixing an aqueous solution of the α- or β-base with an equivalent quantity of the normal salt. The conductivities were then measured, *without the use of any alcohol*, by the methods described above. The molecular conductivities thus determined are set out in Table II.

TABLE II.

Molecular Conductivites of Quadrivalent Tellurium Compounds at 25°.

(*a*) Normal salts.

Compound.	v =	256.	512.	1024.	2048.	4096.
$TeMe_3Cl$	$\Lambda^{25°}$ =	*109*	*111*	*112*	(Bredig)	
,, $+HCl$		*512*	*516*	*517*		
α-$TeMe_2Cl_2$		487	507	512	519	520
,, $-HCl$ ...		*84*	*102*	*107*	*114*	*115*
β-$TeMe_2Cl_2$		487	500	502	509	510
,, $-HCl$ ...		*84*	*95*	*97*	*104*	*105*
α-$TeMe_2Br_2$............		495	503	511	512	513
,, $-HBr$		*90*	*97*	*105*	*106*	*107*
β-$TeMe_2Br_2$............		498	515	515	515	515
,, $-HBr$		*93*	*109*	*109*	*109*	*109*
α-$TeMe_2I_2$			505	510	514	516
,, $-HI$ ...			*100*	*105*	*109*	*111*
β-$TeMe_2I_2$			504	511	526	528
,, $-HI$ ...			*99*	*106*	*121*	*123*
$TeMe_3I$		110	112	116		

TABLE II (*cont.*).

(*b*) Hydroxy-salts.

Compound.	v = 256.	512.	1024.	2048.	4096.
-$TeMe_2(OH)Cl$	103	106	108	111	111
- „	111	117	123	127	131
-$TeMe_2(OH)Br$ ...	107	107·5	111	114	119
- „ ...	113	119	126	131	132
-$TeMe_2(OH)I$	103	107	109	111	111
i- „		122	129	133	136

(c) Free bases.

Compound.	v = 16.	32.	64.	128.	256.	512.	1024.
ι-$TeMe_2(OH)_2$	1·9	2·2	2·6	2·9	3·4	4·3	6·0
3- „	33	34	35	36	37	37	

(a) *Normal salts.* The measurements recorded above showed that the equivalent conductivity of the dihalides, instead of rising to a maximum of 120 or 240, as in the case of a binary or ternary electrolyte, attained to values which exceeded 500. A precedent for these unexpected results was discovered in the molecular conductivities at 25° of the analogous alkyl derivatives of phosphorus, arsenic and antimony (Hantzsch and Hibbert, *Ber.*, 1907, **40**, 1513), some of which are set out below for comparison with the conductivity data of Table II.

	v = 64.	128.	256.	512.	1024.
HBr	402	405	405	406	406
PEt_3Br_2	513·6	535·3	549·5	562·5	565·9
„ −HBr ...	*111·6*	*130·3*	*144·5*	*156·5*	*159·9*
$AsMe_3Br_2$	496·8	510·0	524·7	536·2	559·6
„ −HBr ...	*94·8*	*105·0*	*119·7*	*130·2*	*153·6*
$SbMe_3Br_2$	500·0	509·3	513·2	518·0	521·0
„ −HBr ...	*98·0*	*104·3*	*108·2*	*112·0*	*115·0*
v =	80	160	320	640	1280
$SbMe_3(OH)Br$	201·2	211·8	220·6	231·2	243·9

Since all these abnormalities can be attributed to hydrolysis, we have included in Table II a series of values for the *sum* of the molecular conductivities of trimethyltelluronium chloride and hydrochloric acid, in order to show the order of magnitude of the conductivities that would be produced by complete hydrolysis of one halogen according to the equation $TeMe_2Cl_2 + H_2O \rightleftharpoons TeMe_2(OH)Cl + HCl$. For similar reasons, values are given for the observed molecular conductivities *minus* the molecular conductivity of one molecule of the halogen acid, in order to show how much of the conductivity must be attributed to the hydroxy-halide, on the supposition that one equivalent of halogen has been converted completely into hydrogen halide by hydrolysis. In these calculations, the older values for the equivalent conductivities of the halogen acids were used, since the later values depend on the use of conductivity water of higher quality than could be maintained when the solutions were heated, etc.

(b) *Hydroxy-halides.* The hydroxy-halides are not known in the solid state, since they separate from solution in the form of oxy-salts. Their existence in solution is proved by the facts that (i) when the free bases are titrated with methyl-orange or methyl-red as an indicator, only one molecule of acid is required to neutralise each molecule of base; for example, a solution of the base, which should have been $M/12{\cdot}3$ if a theoretical yield had been obtained, was found to be $N/11{\cdot}6$ when titrated with methyl-orange and $N/12{\cdot}9$ with methyl-red; (ii) the molecular conductivities of these mixed solutions bear no relationship to those of the acid and base from which they were prepared, but have the normal magnitude for a strong binary electrolyte; for example, a solution of the α-base which had been titrated with hydrobromic acid to the point of neutrality to methyl-orange gave the following conductivities:

v =	72	144	288	576	1152	2304
$\Lambda^{25°}$ =	108	112	116	119	121	124

These values have been corrected for the conductivity of the water used for dilution, but are subject to errors arising from the presence of the indicator, and of conducting impurities in the standard acid used for titration. In order to avoid these errors, the solutions for conductivity measurements were prepared by adding an equimolecular solution of the normal salt to a solution of the base which had been standardised by titration. In this way, the halogen content of the solutions was fixed by direct weighing of a crystalline salt, and any uncertainty as to the correct end-point or choice of indicator would only affect the concentration of the weak base with which the salt was mixed. The conductivities of the hydroxy-halides, prepared in this way, are set out in Table II, where they may be compared with Bredig's values for trimethyltelluronium chloride and with our own values for the iodide, $TeMe_3I$. It will be seen that the elimination of the molecule of acid, which is produced by the initial hydrolysis of the normal salts, has had very little effect on the conductivity of the hydroxy-halides, which do not appear to undergo any marked further hydrolysis even when diluted with a large volume of water.

(c) *Free bases.* These were examined in the first instance in order to determine whether they were monoacid bases like potassium hydroxide or diacid bases like barium hydroxide. It was thought that in this way the complications which had arisen from hydrolysis in the study of the normal salts might be avoided. This hope was frustrated, since the conductivities of the free bases were as much *below* those of the ordinary metallic hydroxides as those of the dihalides were *above* the conductivities of the corresponding metallic salts. The conductivities are in fact of the same order as

those of a weak base like ammonia. The two bases are therefore "weak electrolytes" and not (as we had expected) analogous with the completely ionised alkalis; but we are not prepared at present to make any further statement in reference to the strength of the two bases, which we propose to investigate by electrometric methods.

The most striking feature of the preceding measurements is the steadiness of the molecular conductivities both of the normal and of the hydroxy-salts at high dilutions. The limiting value at infinite dilution, towards which the equivalent conductivities of the *normal* salts tend, is not that of *two* molecules of the halogen acid and *one* molecule of the free base (which would give a limiting value $\Lambda_{\infty}^{25^\circ} > 800$), but agrees very well with that of *one* molecule of acid with *one* molecule of the hydroxy-salt (say $\Lambda^{25^\circ} = 405 + 120$). The narrow range of molecular conductivities (from $\Lambda^{25^\circ} = 490$ to 520 at $v = 256$ to 4096) shows that, whereas the *first* halogen is hydrolysed with extraordinary ease and completeness even in the more concentrated aqueous solutions, the *second* is not hydrolysed to any appreciable extent even in the most dilute solutions. The hydrolysis of both halogens, which Vernon represented by the equation $TeMe_2I_2 + 2H_2O = TeMe_2(OH)_2 + 2HI$, does not appear to take place to any marked extent even on extreme dilution. More remarkable still is the fact that no appreciable hydrolysis occurs when the equivalent of halogen acid, which is set free in the first stage of hydrolysis, is removed from the solution. This is proved by the fact that the molecular conductivities of the hydroxy-halides tend towards a limiting value which agrees very well with that of a typical binary electrolyte, say $\Lambda^{25^\circ} = 100$ to 150, whereas, if the salt were hydrolysed in solution to one molecule of acid and one molecule of base, we should expect to find $\Lambda_{\infty}^{25^\circ} > 400$.

Molecular Structure of Quadrivalent Compounds of Tellurium.

Although the facts set out above have been established by a complete series of duplicate determinations with new materials, the interpretation to be put upon them has already become a matter of controversy, since the reading of the paper has been followed by two alternative suggestions as to the formulation of the quadrivalent compounds now under consideration. The point at issue refers to the size of the electron shell, which (including one "lone pair" of unshared electrons) would contain 10 electrons in a 4-covalent compound $[TeX_4]$, 8 electrons in a 3-covalent compound $[TeX_3]X$, and 6 electrons in a 2-covalent compound $[TeX_2]X_2$.*

* The series need not be carried further, since the compounds now under consideration all contain two methyl groups attached to the metal.

(i) *Ten-electron shells.* Sidgwick states that tellurium "has been proved to give 4-covalent compounds in which all the groups lie in a plane" ("Electronic Theory," p. 231); but it is not obvious on what facts the "proof" of this statement depends, since quadrivalent tellurium differs from tin and lead mainly in that it does *not* form any quadricovalent compounds to correspond with tin tetraethyl or lead tetraethyl. For instance, of a series of 26 alkyl and aryl derivatives of tellurium prepared by Lederer (*Compt. rend.*, 1910, **151**, 611; *Ber.*, 1911, **44**, 2287; 1916, **49**, 1615, *et seq.*; *Annalen*, 1912, **391**, 326) not a single one contains more than three of these radicals (compare also Morgan and Burgess, this vol., p. 321). This fact provides *a priori* evidence that the expansion of the octet into a 10-electron shell * is a difficult operation, and warns us to look with suspicion on any formula in which this configuration is postulated, especially with radicals which can be ionised more readily than methyl. The fact that the trialkyltelluronium halides $[TeR_3]X$ are "strong electrolytes," like $[NMe_4]Cl$, provides further evidence that the formation of a fourth bond is resisted by the greater stability of the octet as compared with a 10-electron shell; it would indeed be unreasonable to expect that a halogen ion, which already carries a complete octet, should force its way into the complete octet of an atom of tellurium, which cannot provide an additional bond to hold a fourth alkyl group.

(ii) *Eight-electron shells.* In order to maintain the octet rule when four covalent 2-electron bonds would lead to a shell of 10 electrons, Sugden has suggested (*Chem. and Ind.*, 1927, **46**, 540) that the halogen may be held to the metal by 1-electron bonds, as in the formula $\frac{Me}{Me}\!>\!Te\!<\!\frac{I}{I}$. Since the evidence for these pairs of 1-electron bonds, even in the cases of phosphorus pentachloride and antimony pentachloride, rests upon a theoretical interpretation of the parachor (which has not yet been confirmed by experiment), this formula may be regarded merely as an alternative scheme for attaching both halogens to the metal to form a covalent molecule, and so enabling the salts to function as "weak electrolytes." † If, however, we wish to maintain both the duplet and the octet in this series of compounds, we are limited to a formula, $[TeMe_2X]X$, which embodies the novel

* The formation of a 12-electron shell in sexavalent compounds such as sulphur hexafluoride and tellurium hexafluoride is not disputed; and the quadricovalency already postulated in the "sexavalent" *oxy-compounds* of sulphur (*Trans. Faraday Soc.*, 1923, **18**, 289), can obviously occur also in the analogous compounds of tellurium.

† For a discussion whether the small conductivity of certain salts in non-aqueous solvents is due to covalent molecules, strongly deformed ions, or ion pairs, see Ulich (*Trans. Faraday Soc.*, 1928, **24**, 27).

characteristic that, although both halogens may be ionisable in turn, only one of them can be ionised at a time. Thus, we may write the hydroxy-halides as $[TeMe_2X]OH$, in which case they would be *bases* like $[TeMe_3]OH$, or as $[TeMe_2\cdot OH]X$, in which case they would be binary *salts*. A given molecule could then have the structure either of a base or of a salt, and could probably exercise both functions alternately; but it could not split off a hydroxyl and a halogen ion simultaneously, except by forming an unstable 6-electron shell.

(iii) *Six-electron shells.* Finally, the dihalides may be regarded as salts of a diacid base, and formulated as $[TeMe_2]X_2$. This is the most plausible way of expressing Vernon's statement that "both atoms of halogen are ionisable," although (as was natural at the time when his papers were published) he did not make any distinction between polar and non-polar bonds.

(a) *Hydroxy-halides.*—In discussing the molecular structure of this series of compounds, it is convenient to consider first the α-hydroxy-halides on account of the very close analogies which they present with the trimethyltelluronium halides.

(i) The hydroxy-halides behave as *neutral* salts which, prepared as described above, are not hydrolysed to any large extent, even at the highest dilutions.

(ii) They also behave as *strong electrolytes*. For example, whereas the chloride, $TeMe_3Cl$, gives $\Lambda^{25°} = 103$ to 112 at $v = 64$ to 1024, and the iodide, $TeMe_3I$, gives $\Lambda^{25°} = 110$ to 116 at $v = 256$ to 1024, the three α-hydroxy-halides give values for $\Lambda^{25°}$ ranging from 103 to 119 at $v = 256$ to 4096. The conductivities of the salts also appear to be additive functions of those of their ions, since they can be interpreted on the assumption that the ion $[\alpha\text{-}TeMe_2\cdot OH]^+$ has a mobility of about the same magnitude as $[TeMe_3]^+$, the slightly higher conductivity of the bromide being in agreement with the slightly greater mobility of the bromide ion as compared with the chloride and iodide ions.

(iii) This additive relationship also extends to the *colour* of the solutions, since the striking contrast which exists between the absorption spectra of the unhydrolysed dihalides, when examined in alcoholic solutions, disappears when these compounds are hydrolysed to the corresponding hydroxy-halides by dissolution in water. In particular, the "iodoform band," which distinguishes the di-iodides from the dibromides and dichlorides, is entirely lacking in the case of the α-hydroxyiodide, which gives only a general absorption ($\log \epsilon = 2\cdot5$ at 2600 Å.) of about the same intensity as that of the dichlorides.

The β-hydroxy-halides also behave as *strong electrolytes* and

neutral salts, which do not undergo any marked hydrolysis in solution. The slightly higher conductivities of the β-salts shown in Table II cannot be attributed to unequal mobility of the kations $[\alpha\text{-TeMe}_2\cdot\text{OH}]^+$ and $[\beta\text{-TeMe}_2\cdot\text{OH}]^+$, since this difference should appear also in the conductivities of the hydrolysed normal salts. We suspect that it may depend on some small difference in the end-point when two weak bases of unequal strength are being titrated; but this difference is not large enough to affect any of the arguments that are used in the present paper. Since, therefore, both series of hydroxy-halides behave as neutral, strong electrolytes, we have no hesitation in assigning to them the general formula * $[\overset{+}{\text{Te}}\text{Me}_2\cdot\text{OH}]\overset{-}{\text{X}}$.

(*b*) *Dihalides*.—The study of the dihalides is rendered difficult by the fact that they are hydrolysed almost completely by water, even when an excess of free acid is present; it has therefore been impracticable to determine the conductivity of the unhydrolysed salt by Schilow's method of using a dilute acid as solvent. As we have no direct knowledge of the conductivity of the dihalides in aqueous solutions, we can only speculate that, since no important change of conductivity is produced when CH_3 is replaced by OH (although this involves the replacement of a "positive" by a "negative" radical), the further replacement of OH by Cl, Br or I would not be likely to alter the conductivity in any fundamental way; in particular, the introduction of a second easily ionised radical would not be likely to impede the ionisation of the salt to such an extent as to convert the strong electrolyte into a weak electrolyte or a non-electrolyte, if it could be examined in water in an unhydrolysed state. Mere analogy therefore suggests that the dihalides should be formulated after the model of the trimethyl- and hydroxy-halides, as $[\text{TeMe}_2\text{X}]\text{X}$; this is also in harmony with the formulation of the α-tetraiodide as $[\text{TeMe}_2\text{I}]^+\text{I}_3^-$.

This unsymmetrical formula is the only one which will account simultaneously for the colour of the salts and for their conductivity in a medium such as acetonitrile; but, if *two* formulæ are assigned to each compound, it is obviously possible to use the 10-electron formula to account for the colour, and the 6-electron formula to account for the ionisation of the dihalides; or we may postulate a dynamic equilibrium between the form represented by the unsymmetrical octet formula, $[\text{TeMe}_2\text{X}]\text{X}$, and a valency-isomeride represented by Sugden's symmetrical octet formula. These alternative hypotheses, however, all involve an increase in the number of

* It is, however, possible that the neutral hydroxyl groups may give rise even in aqueous solution, to oxides similar to those which are formed when the solutions are evaporated to dryness.

arbitrary variables that are used to express the behaviour of the salts and we are not yet convinced that this is necessary. Thus the hypothesis that both halogens are ionisable simultaneously could only be justified by evidence, which we have not yet found, that the salts (or the bases from which they are derived) can behave as ternary electrolytes; and, although the dissimilar behaviour of the two halogens towards water does not afford positive proof of the unsymmetrical formula (since a similar contrast exists between the behaviour of two halogens in $\alpha\alpha'$-dibromocamphor, where no difference of linkage need be suspected), it is nevertheless of vital importance, because, if no more contrast had been found than that which exists between the two halogens of calcium chloride or methylene iodide, there would be no justification for placing one atom inside the bracket and the other outside. Actually, however, the contrast is quite as well marked as in many of the co-ordination compounds in which this distinction is made. Whilst, therefore, we are ready to admit the possible validity under various conditions of the symmetrical formulæ of Sidgwick, Sugden, and Vernon, we feel free to regard them as still unproved.

(c) *Bases.*—In contrast to the dihalides and the hydroxy-halides, the free bases are very poor conductors. The reversibility of their ionisation can, however, be explained quite readily, as in the case of ammonia, either by the formation of anhydrides, such as is already known to occur in the case of the hydroxyhalides, thus $[\overset{+}{T}eMe_2{\cdot}OH]\overset{-}{O}H \rightleftharpoons [\overset{+}{T}eMe_2\overset{-}{O}] + H_2O$, or by the co-ordination of the hydroxyl ion with an atom of hydrogen inside the bracket. The formation of a 4-covalent compound $[TeMe_2(OH)_2]$ is another alternative, which we should hesitate to adopt until some independent proof is available of the existence of 4-covalent derivatives of quadrivalent tellurium.

Summary.

(*a*) Measurements have been made of the extinction coefficients and molecular conductivities of Vernon's dimethyltelluronium dihalides. The close resemblance which Vernon observed between the α- and β-compounds is confirmed by these observations.

(*b*) The α- and β-dichlorides show only general absorption, but the dibromides show a marked step-out; the α- and β-di-iodides show the twin maxima already recorded for iodoform and potassium tri-iodide. These two maxima also appear, with an enhanced intensity, in the α-tetraiodide, to which the formula $[\overset{+}{T}eMe_2I]\overset{-}{I}_3$ is assigned. The spectroscopic evidence indicates that a similar formula may be assigned to the dihalides.

(*c*) Instead of behaving as binary or ternary electrolytes in

aqueous solution, the dihalides give conductivities which indicate that one halogen atom is hydrolysed more or less completely and the other atom forms a halogen ion, *e.g.*, $[\overset{+}{Te}Me_2Cl]\overset{-}{Cl} + H_2O \rightleftharpoons [\overset{+}{Te}Me_2{\cdot}OH]\overset{-}{Cl} + \overset{+}{H}\overset{-}{Cl}$. The hydroxy-halides produced by this hydrolysis are strong electrolytes which are not hydrolysed to any large extent even when the equivalent of acid shown in the preceding equation is removed. The free bases, on the other hand, which can be prepared only with the help of silver oxide, are weak electrolytes, like ammonia.

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CAMBRIDGE. [*Received, October 17th*, 1927.]

XLIV.—cyclo*Telluropentane.*

By GILBERT T. MORGAN and HENRY BURGESS.

AN investigation of the interactions of tellurium tetrachloride and acetylacetone by one of us (G. T. M.) and H. D. K. Drew led in 1921 to the discovery of *cyclo*telluripentane-3 : 5-dione 1 : 1-dichloride (I) and *cyclo*telluropentane-3 : 5-dione (II), these substances being the simplest members of two new series of organo-metalloidal compounds in both of which tellurium is implicated in a six-membered ring (J., 1920, **117**, 1456; 1923, **123**, 444; 1924, **125**, 731, 1601; *J. Soc. Chem. Ind.*, 1924, **43**, 40, 304).

$$\text{(I.)}\quad CH_2{<}{CO{\cdot}CH_2 \atop CO{\cdot}CH_2}{>}TeCl_2 \longrightarrow CH_2{<}{CO{\cdot}CH_2 \atop CO{\cdot}CH_2}{>}Te \quad \text{(II.)}$$

The series containing bivalent tellurium are yellow compounds sparingly soluble in cold water, and in collaboration with E. A. Cooper it was found that these aqueous solutions had considerable bactericidal potency in broth media (Morgan, Drew, and Cooper, J., 1922, **121**, 923; *Biochem. J.*, 1923, **17**, 30), whereas this intense germicidal action diminished very considerably when the compounds were employed in serum (*Biochem. J.*, 1924, **18**, 190).

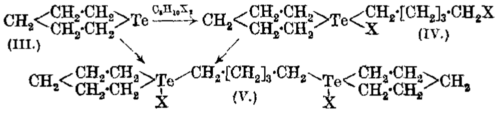
On account of the noteworthy chemical and bacteriological properties of the new cyclic tellurium derivatives, it became desirable to obtain if possible the non-oxygenated *cyclo*telluropentane (III), which may be regarded as the parent tellurohydrocarbon of the two series (I and II).

Attempts made to prepare the dibromide or di-iodide of *cyclo*-telluropentane by heating tellurium with αε-pentamethylene dibromide or di-iodide gave only small yields of cyclic products even when the amorphous metalloid was prepared, whereas the

dichloride did not interact with tellurium under these conditions. A satisfactory preparation was achieved, however, by condensing a metallic telluride, preferably the aluminium compound, with a αε-pentamethylene dihalide; the *cyclo*telluropentane ring was then produced in accordance with the following equation, which represents this interaction with the dibromide :

$$Al_2Te_3 + 3CH_2Br{\cdot}[CH_2]_3{\cdot}CH_2Br = 3C_5H_{10}{:}Te + 2AlBr_3$$

The tellurohydrocarbon is not, however, isolated at this stage, since it combines additively with more of the alkylene dihalide to form two complex telluronium bromides. The following diagram illustrates the general course of the condensation when X = Cl,Br, or I :



1-ε-*Bromoamyl*cyclo*telluripentane* 1-*bromide* (IV) and *pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*dibromide* (V) both dissolve in water, the latter being the more soluble.

In addition to these complex bromides a small amount of cyclo*telluripentane* 1 : 1-*dibromide*, $CH_2{<}{CH_2{\cdot}CH_2 \atop CH_2{\cdot}CH_2}{>}TeX_2$ (VI), is produced during the condensation, probably through the interaction of moisture unavoidably introduced during the reaction; the unstable hydrogen telluride thereby set free readily furnishes amorphous tellurium, which interacts with pentamethylene dibromide. This dibromide (VI) is, however, more readily prepared by adding the calculated amount of bromine to the mixture of *cyclo*telluropentane and αε-pentamethylene dibromide produced by the thermal dissociation of the foregoing two complex telluronium bromides when these salts are heated under reduced pressure.

The condensation with aluminium telluride and αε-pentamethylene dichloride takes a similar course, except that no *cyclo*telluripentane dichloride is formed and a little *cyclo*telluropentane is detected by its odour and by the presence of its solid oxidation product (*cyclo*telluripentane oxide).

The complex telluronium salts, 1-ε-*chloroamyl*cyclo*telluripentane* 1-*chloride* (IV) and *pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*dichloride* (V), resemble the corresponding bromides, but are more readily soluble in water and the alcohols. cyclo*Telluripentane* 1 : 1-*dichloride* (VI) is prepared by adding chlorine to the foregoing

complex chlorides or to the products of their thermal dissociation. cyclo*Telluropentane* (III), prepared by the reduction of *cyclo*telluripentane 1 : 1-dibromide with aqueous alkali metabisulphite (Morgan and Drew, *loc. cit.*), is so readily oxidised in air that it must be distilled in an inert atmosphere, being thus obtained as a light yellow oil which assumes a reddish-orange tint on exposure to light even in a sealed tube. It is more stable towards reducing agents than are the *cyclo*telluropentane-3 : 5-diones, since there is very little tellurium eliminated during the reduction of the dibromide with bisulphite.

The condensation between aluminium telluride and the $\alpha\epsilon$-pentamethylene dihalides follows a well-marked gradation, the di-iodide reaction taking place most readily, whereas the dichloride reaction requires the highest temperature.

The tendency to form the simple *cyclo*telluripentane dihalides (VI) increases with the atomic weight of the halogen. A similar gradation of properties was observed in regard to recombination of the products of the thermal dissociation of the three 1-ϵ-halogeno-amyl*cyclo*telluripentane 1-halides. The chloro-compound (IV) when melted in a sealed tube shows no disposition to resolidify on further heating, whereas in these circumstances both the bromo- and the iodo-derivative resolidify.

*cyclo*Telluripentane 1 : 1-di-iodide (VI), produced by direct addition of iodine to *cyclo*telluropentane in carbon tetrachloride, exists in two differently coloured forms: (α) a deep red modification with a purple-blue reflex, this variety being stable at the ordinary temperature in the presence of light, and (β) an orange modification which separates from hot solvents and passes slowly into the deep red form at the ordinary temperature, especially when exposed to light. The deep red modification crystallises from cold solutions, although occasionally it is accompanied by crystals of the orange form.

Bactericidal Action of cyclo*Telluropentane Derivatives.*

For the following preliminary bacteriological data we are indebted to Dr. H. Barnes.

The complex bromides (IV and V) have only slight bactericidal action, whereas *cyclo*telluropentane and *cyclo*telluripentane 1 : 1-dibromide and dichloride (VI) are considerably more potent and give approximately the same bactericidal coefficient with *Bacillus coli*, a result which indicates that in these cases the active agent is *cyclo*telluripentane 1 : 1-dihydroxide, produced either by hydrolysis of the dihalides or by wet oxidation of *cyclo*telluropentane. This bactericidal value is considerably less than the coefficients obtained

with the *cyclo*telluropentane-3 : 5-dione series, but, unlike the latter, it is far less affected in serum, a result which is sufficiently promising to merit further investigation.

EXPERIMENTAL.

Although tellurium has been shown to combine with methyl iodide to form dimethyltelluronium di-iodide (Demarçay, *Bull. Soc. chim.*, 1883, **40**, 99; Scott, P., 1904, **20**, 157; Vernon, J., 1920, **117**. 86, 889), yet the corresponding reaction with pentamethylene di-iodide only occurred to a slight extent. When either pentamethylene di-iodide or dibromide was heated in xylene with amorphous tellurium for 20 hours, a 10% yield of the corresponding *cyclo*telluripentane dihalide was obtained and about 80% of the tellurium was recovered unchanged. The powdered metalloid seemed to be quite as effective in the case of the polymethylene di-iodide, but no cyclic compound was formed with the dibromide under various conditions. Owing to the small yield in these experiments recourse was had to the condensation taking place between the αε-pentamethylene dihalides and metallic tellurides (Morgan and Burgess, E. P. 7030 of 1927).

Pentamethylene di-iodide was prepared by refluxing the corresponding dibromide with a 15% solution of anhydrous sodium iodide in dry acetone for 1 hour. The sodium bromide was filtered off and the liquid fractionated in a vacuum (yield, 90% of the theoretical).

Aluminium telluride (27 g.) and pentamethylene dibromide (63·5 g.) were heated under reflux until at 165° (approximately) a reaction ensued which caused the dibromide to boil vigorously. This ebullition was moderated by cooling and stirring, and the heating was subsequently continued for 1 hour. The semi-solid product was then extracted successively with (*a*) carbon tetrachloride to remove unchanged pentamethylene dibromide and most of the *cyclo*telluripentane 1 : 1-dibromide; (*b*) moist acetone to dissolve the remaining *cyclo*telluripentane 1 : 1-dibromide, and 1-ε-bromoamyl*cyclo*telluripentane 1-bromide, this solvent also extracting some of the pentamethylene-αε-bis*cyclo*telluripentane 1 : 1′-dibromide and aluminium bromide; (*c*) water or moist methyl alcohol to extract the remainder of the aluminium bromide and bis*cyclo*telluri-compound from a dark grey, insoluble residue (6·7 g.). By fractional crystallisation of the three extracts the following yields of organic tellurium derivatives were obtained: (IV), 14 g.; (V), 23 g.; (VI), 2 g. The proportion of (VI) was always small, but the relative amounts of (IV) and (V) were variable, the yield of (IV) being diminished on decreasing the proportion of

pentamethylene dibromide. If, however, the quantity of this reagent was diminished by one-third, the amount of insoluble residue was increased considerably. When magnesium telluride was employed in the condensation, the reaction commenced only at 200° (approximately) and the yield of soluble organo-tellurium derivatives was comparatively small.

Condensations with αε-pentamethylene dichloride and aluminium telluride were less vigorous, a higher temperature (175—185°) being required to start the reaction. Two tellurichlorides only were obtained (corresponding with IV and V), but the presence of *cyclo*telluripentane 1 : 1-dichloride was not detected, although the carbon tetrachloride extract indicated by its odour, colour, and deposition of solid oxidation product that free *cyclo*telluropentane was formed during the condensation.

Owing to the greater solubilities of the two organic tellurichlorides, their separation from aluminium chloride was less complete than that of the corresponding bromides from aluminium bromide. In extractions of the chlorides ethyl alcohol as the third solvent was more favourable than water.

1. cyclo*Telluripentane Chlorides.*—cyclo*Telluripentane* 1 : 1-*dichloride* (VI), prepared by the dissociation method from 1-ε-chloroamyl*cyclo*telluripentane 1-chloride (compare p. 323), crystallised from carbon tetrachloride in six-sided prisms, m. p. 106—107° (Found: Te, 46·9, 46·95; Cl, 26·4. $C_5H_{10}Cl_2Te$ requires Te, 47·5; Cl, 26·4%). This dichloride was also prepared by the direct addition of a slight excess of chlorine to 1-ε-chloroamyl*cyclo*telluripentane 1-chloride.

With sodium dichromate in aqueous solution, the dichloride yielded a dichromate crystallising from hot water in rosettes of *yellow* needles, which are less photosensitive than the other complex dichromates described below.

*1-ε-Chloroamyl*cyclo*telluripentane 1-chloride* (IV) resembled the corresponding bromide, but was generally more soluble than the latter; it melted at 149—151° (Found: Te, 37·7; Cl, 20·8. $C_{10}H_{20}Cl_2Te$ requires Te, 37·65; Cl, 20·95%). When heated under reduced pressure, it dissociated into *cyclo*telluropentane and pentamethylene dichloride. With aqueous sodium dichromate, it gave a yellow, oily precipitate darkening on exposure to light.

*Pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*dichloride* (V) was much more soluble in the alcohols than the corresponding bromide; it crystallised from ethyl alcohol, containing hydrochloric acid, in anhydrous prisms, decomp. 224—225° (Found: Te, 47·3; Cl, 13·3. $C_{15}H_{30}Cl_2Te_2$ requires Te, 47·5; Cl, 13·2%). The aqueous solution gave at first a faint precipitate with silver nitrate, which slowly increased.

The mother-liquor from the crystallisation of the complex dichlorides, when precipitated fractionally with aqueous sodium dichromate, gave in succession two deposits. The second was crystalline and consisted of *pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1'-*dichromate*, which crystallised from hot water in rosettes of daffodil-yellow plates, turning brown at 160° and decomposing at 193° (Found : Te, 36·2. $C_{15}H_{30}O_7Te_2Cr_2,H_2O$ requires Te, 36·5%). This dichromate was very sensitive to light, rapidly becoming brown on exposure.

2. cyclo*Telluripentane Bromides.*—cyclo*Telluripentane* 1 : 1-*dibromide* (VI), obtained as a by-product in the condensation between aluminium telluride and αε-pentamethylene dibromide, was more conveniently prepared by heating either of the two following substances to 160—190° under 25—30 mm. pressure. Thermal dissociation led to cyclotelluropentane and pentamethylene dibromide, with elimination of water in the case of the hydrated telluribromide. The cooled yellow distillate was diluted with carbon tetrachloride and treated with bromine in excess; *cyclo*telluripentane dibromide then slowly separated and was crystallised successively from benzene and carbon tetrachloride (yield, 90%) (Found: Te, 35·3; Br, 44·75; C, 16·8; H, 3·1. $C_5H_{10}Br_2Te$ requires Te, 35·7; Br, 44·7; C, 16·8; H, 2·8%).

*cyclo*Telluripentane 1 : 1-dibromide crystallised from carbon tetrachloride in pale greenish-yellow prisms or from light petroleum in hexagonal plates; it melted at 105—107°. It dissolved readily in benzene, chloroform, or acetone, but only sparingly in cold alcohol, carbon tetrachloride, or light petroleum. Hot water hydrolysed the dibromide, giving an acid solution, but nothing separated on cooling.

*cyclo*Telluripentane 1 : 1-dibromide was also formed by mixing carbon tetrachloride solutions of 1-ε-bromoamyl*cyclo*telluripentane 1-bromide and bromine (1·6 mols.). A heavy, red oil separated, from which petroleum or methyl alcohol extracted the dibromide.

1-ε-*Bromoamyl*cyclo*telluripentane* 1-*bromide* (IV) was readily soluble in oxygenated organic solvents, in chloroform and in water. The aqueous solution was faintly acid to litmus and gave an immediate precipitate with silver nitrate. This telluripentane bromide crystallised from acetone in colourless, oblong plates, m. p. 143—145°, resolidifying at 147° (Found: Te, 29·75; Br, 36·8; C, 27·9; H, 4·9. $C_{10}H_{20}Br_2Te$ requires Te, 29·8; Br, 37·4; C, 28·1; H, 4·7%).

*Pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1'-*dibromide* (V) was readily soluble in water, less soluble in the alcohols, and almost insoluble in other organic solvents; it crystallised in colourless

needles containing $1H_2O$ and decomposed at 223—224° (Found for hydrate: C, 27·75; H, 5·1. $C_{15}H_{30}Br_2Te_2,H_2O$ requires C, 28·0; H, 5·0%. Found for dried salt: Te, 40·55, 40·8; Br, 25·3. $C_{15}H_{30}Br_2Te_2$ requires Te, 40·8; Br, 25·6%).

The aqueous solution of the complex dibromide was neutral to litmus and gave with silver nitrate a faint precipitate which rapidly increased.

*Pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*bisperbromide*, $C_5H_{10}[Te(C_5H_{10})Br_3]_2$.

Bromine (2·2 mols.) in carbon tetrachloride was added to a suspension of the foregoing compound in chloroform, and the mixture heated for 30 minutes. The colour of bromine faded rapidly with the separation of a dark red oil which solidified on cooling; m. p. 102—104° (Found: Te, 26·3; Br, 49·9. $C_{15}H_{30}Br_6Te_2,H_2O$ requires Te, 26·5; Br, 49·8%). This product was insoluble in all organic media except acetone, in which it decomposed with generation of a lachrymatory vapour (possibly that of bromoacetone).

3. cyclo*Telluropentane*.—Potassium metabisulphite (25 g.), dissolved in 150 c.c. of water, was added in two equal portions, with a 20 minutes' interval, to 20 g. of powdered *cyclo*telluripentane 1 : 1-dibromide, the mixture being well stirred. The dibromide changed gradually to a dark red oil. After being shaken for 1½ hours, the oily mixture was extracted with chloroform, the dried extract evaporated in a current of hydrogen to remove the solvent and distilled under reduced pressure, and the distillate rectified with the exclusion of air (Found: Te, 64·0, 64·3; C, 30·0, 30·7; H, 5·3, 5·2. $C_5H_{10}Te$ requires Te, 64·5; C, 30·4; H, 5·1%).

Although very little tellurium was eliminated during the reduction of the dibromide, yet a considerable proportion of red, non-volatile residue was left after distillation of the *cyclo*telluropentane; this residue, which blackened on heating, was not investigated further.

cyclo*Telluropentane* was thus obtained as a lemon-yellow oil having an extremely unpleasant alliaceous odour recalling that of trimethylstibine; it boiled at 82—83°/12 mm. and at 44—45°/1—2 mm. It was oxidised rapidly in air to a colourless solid and reacted violently with fuming nitric acid. When kept for several weeks in a sealed tube, it gradually assumed a reddish-orange colour, the change being accelerated by light.

cyclo*Telluripentane* 1 : 1-*dioxide*, $CH_2{<}{CH_2{\cdot}CH_2 \atop CH_2{\cdot}CH_2}{>}Te{\lessgtr}{O \atop O},H_2O$, was obtained as a white, amorphous powder on addition of hydrogen peroxide to *cyclo*telluropentane dissolved in warm methyl alcohol (Found: Te, 50·3. $C_5H_{10}O_2Te,H_2O$ requires Te, 51·5%).

This insoluble product, which exploded on rapid heating, darkened at about 195°; it had the properties of a tellurone, liberated chlorine from hydrochloric acid, decolorised warm acidified permanganate, and decomposed violently on treatment with concentrated nitric or sulphuric acid.

4. cyclo*Telluripentane Di-iodides.*—Aluminium telluride (5·5 g.) and αε-pentamethylene di-iodide (22 g.; 1·8 mols.) interacted smoothly when heated at 135—145° for 1 hour. The product was cooled and extracted with (*a*) benzene, (*b*) acetone, (*c*) methyl alcohol, and (*d*) water, leaving a black, insoluble residue (0·75 g.). The yields of (IV), (V), and (VI) were 3·5 g., 3·4 g., and 1·7 g., respectively, 4·5 g. of pentamethylene di-iodide being recovered unchanged.

1-ε-*Iodoamyl*cyclo*telluripentane* 1-*iodide* (IV) crystallised in colourless flakes, melted at 135—136°, resolidified almost immediately, and remelted at 197—198°. It dissolved slightly in hot water, giving a neutral solution (Found: I, 48·2. $C_{10}H_{20}I_2Te$ requires I, 48·7%).

*Pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*di-iodide* (V) crystallised from hot water in rosettes of brownish-yellow, acicular prisms, m. p. 216—217° (decomp.). It dissolved in boiling water to give an alkaline solution (Found: I, 35·6. $C_{15}H_{30}I_2Te_2$ requires I, 35·3%). Aqueous solutions of both these iodides give a transient yellow coloration with silver nitrate and no immediate precipitation of silver iodide. A slow precipitation occurs on boiling, the speed of this being greater in the case of the latter compound. Both compounds resemble the corresponding chlorides and bromides, but their solubilities are considerably less.

cyclo*Telluripentane* 1 : 1-*di-iodide*, obtained as a by-product in the foregoing condensation, is prepared preferably by adding iodine in slight excess to *cyclo*telluropentane in carbon tetrachloride. The product was obtained in two kinds of crystals: (α) Deep red prisms with purple-blue reflex (Found: Te, 28·1%); (β) highly refractive, slender, orange prisms (Found: I, 55·9. $C_5H_{10}I_2Te$ requires Te, 28·2; I, 56·2%). On exposure to light the orange form, which separated from hot solutions, was transformed into the dark red crystals within 2 days. A slower change took place in the dark. Molecular-weight determinations in hot and in cold benzene gave *M* (cryoscopic) 414, 418; (ebullioscopic) 453, 465, 473 ($C_5H_{10}I_2Te$ requires *M*, 451).

These data exclude polymerism, whereas the deepening of colour which occurred when the solutions of the di-iodides were heated suggests that the difference between the two modifications goes further than dimorphism. More experimental work would, how-

ever, be required to establish that the difference is a case of isomerism.

Dr. T. V. Barker has kindly supplied the following additional information regarding the two differently coloured forms: "Neither modification is suitable for exact angular measurements. Under the polarising microscope, the stable modification (with purple-blue reflex) is strongly dichroic, appearing light or dark red, according as the vibrations are along or across the direction of elongation. A biaxial figure is seen in convergent light with one optic axis nearly normal to the predominant face. The needles of the yellow modification show a corresponding light and dark yellow dichroism. The extinction also is straight with negative elongation, but no optic figure is visible."

The two forms of *cyclo*telluripentane 1 : 1-di-iodide were less soluble than the corresponding chloride or bromide. Both varieties melted at 135—136°, the purple crystals first becoming orange at 105°. A benzene or carbon tetrachloride solution of either form became reddish-orange on boiling and resumed a light orange tint on cooling.

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TEDDINGTON, MIDDLESEX. [*Received, December 15th, 1927.*]

XLV.—*Nitrosation of Phenols. Part V. Preparation of an* o-*Nitrosophenol.*

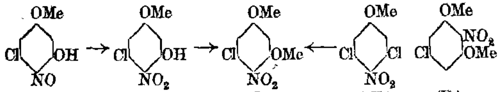
By HERBERT HENRY HODGSON and JOHN SAMUEL WIGNALL.

NITROSATION of 5-chloro-3-hydroxyanisole proceeds readily (compare 3 : 5-dichlorophenol; J., 1927, 2216). The constitution of the product (I) was proved by oxidation to the *nitro*-compound (II), the methyl ether of which was identical with *5-chloro-4-nitro-resorcinol dimethyl ether* (III), prepared by the action of sodium methoxide on 3 : 5-dichloro-4-nitroanisole (IV). The directive power of the methoxyl group in 5-chloro-3-hydroxyanisole has therefore completely overcome the para-directing influence of the chlorine atom.

The nitroso-formula is preferred to the quinone-oxime formula for *5-chloro-4-nitroso-3-hydroxyanisole* (I) on account of its deep green colour and low m. p. (compare Hodgson and Moore, J., 1925, **127**, 2260).

3 : 5-Dichloro-2-nitroanisole reacts readily with sodium methoxide to give *5-chloro-2-nitroresorcinol dimethyl ether* (V); the reactivity of the 3-chlorine atom contrasts strongly with the

stability of the halogen in 3-chloro-2-nitroanisole (Hodgson and Handley, J., 1926, 542).



(I.) (II.) (III.) (IV.) (V.)

Unlike 3 : 5-dichlorodimethylaniline, *5-chloro-3-methoxydimethylaniline* is readily nitrosated. The product is probably 5-chloro-4-nitroso-3-methoxydimethylaniline, but on boiling with dilute alkali solution it gives, not the expected 5-chloro-6-nitroso-3-hydroxyanisole, but products of profound decomposition.

EXPERIMENTAL.

5-Chloro-4-nitroso-3-hydroxyanisole (I).—A solution of 5-chloro-3-hydroxyanisole (8 g.) in water (900 c.c.) containing sodium hydroxide (2·5 g.) and sodium nitrite (20 g.) was cooled to 0°, and sulphuric acid (6 g. of 98% acid in 30 c.c. of water) added during 2 hours. The *5-chloro-4-nitroso-3-hydroxyanisole*, obtained in almost theoretical yield after 6 hours, crystallised from methyl alcohol in deep green needles, m. p. 132° (decomp.) (Found: Cl, 18·9. $C_7H_6O_3NCl$ requires Cl, 18·9%), which are insoluble in light petroleum, slightly soluble in benzene, alcohol, carbon tetrachloride, and water, and moderately easily soluble in acetone, ether, and glacial acetic acid. The nitroso-compound does not respond to the Liebermann nitrosoamine test, gives a Bordeaux-red colour in concentrated sulphuric acid, is not affected by hot *N*-hydrochloric acid but is decomposed by the hot concentrated acid. From its deep green solution in 10% aqueous sodium hydroxide it is precipitated unchanged on acidification; hot concentrated alkalis decompose it.

5-Chloro-4-nitro-3-hydroxyanisole (II) was obtained by dissolving 5-chloro-4-nitroso-3-hydroxyanisole (3·3 g.) in a hot solution of potassium hydroxide (1 g.) in water (50 c.c.) and then adding potassium hydroxide (9 g. in 20 c.c. of water), followed by finely powdered potassium ferricyanide (17·5 g.); the whole was kept at 60° for about 3 hours until the colour changed from deep green to orange. (This procedure is necessary to avoid the decomposition referred to above.) The mixture was then faintly acidified and the *5-chloro-4-nitro-3-hydroxyanisole* (2·2 g.) removed by steam distillation. The product crystallised from dilute methyl alcohol in light golden needles, m. p. 105° (Found: Cl, 17·2. $C_7H_6O_4NCl$ requires Cl, 17·4%), which are only slightly soluble in water and light

petroleum but very soluble in carbon tetrachloride, chloroform, ether, benzene, and glacial acetic acid. It gives a red colour with sulphuric acid and an orange solution in aqueous sodium hydroxide.

Nitration of 5-Chloro-3-hydroxyanisole.—A solution of the chloro-hydroxyanisole (4 g.) in water (80 c.c.) containing sodium nitrate (3 g.) was treated at 100° with a mixture of sulphuric acid (98%, 3 c.c.) and water (20 c.c.), added gradually during 1 hour. After remaining for 2 hours at 100°, the bulk of the initial material was recovered unchanged, but distillation with steam gave a small quantity of 5-chloro-4-nitro-3-hydroxyanisole, identical with the compound described above.

5-Chloro-4-nitroresorcinol dimethyl ether (III) was prepared by treating either of the above products in boiling xylene with excess of methyl sulphate in presence of potassium carbonate. It crystallised from methyl alcohol in light yellow needles, m. p. 123° (Found Cl, 16·1. $C_8H_8O_4NCl$ requires Cl, 16·3%).

Action of Sodium Methoxide on (a) *3 : 5-Dichloro-2-nitroanisole and* (b) *3 : 5-Dichloro-4-nitroanisole.*—2- and 4-Nitro-3 : 5-dichlorophenols were prepared by a modification of Hodgson and Wignall's method (J., 1927, 2218), the resinous nitration product from 3 : 5-dichlorophenol being separated from the acid liquor, washed free from acid, and very slowly steam-distilled. 3 : 5-Dichloro-2-nitrophenol then passed over as a colourless solid, which, on heating or on exposure to air, was transformed into the lemon-yellow anhydrous substance previously described (*loc. cit.*), the change indicating the existence of a hydrate similar to, although more labile than, that formed by 3-chloro-2-nitrophenol (Hodgson and Moore, J., 1926, 155).

(*a*) A mixture of 3 : 5-dichloro-2-nitroanisole (2·2 g.) and sodium methoxide (methyl alcohol, 18 c.c.; sodium, 0·8 g.) was gently boiled under reflux for 4 hours. *5-Chloro-2-nitroresorcinol dimethyl ether* (V) was deposited on cooling. It crystallised from methyl alcohol in colourless needles, m. p. 171° (Found: Cl, 16·0. $C_8H_8O_4NCl$ requires Cl, 16·3%), and was less soluble in most solvents than the 4-nitro-isomeride (below).

(*b*) Similar treatment of 3 : 5-dichloro-4-nitroanisole gave a substance identical with 5-chloro-4-nitroresorcinol dimethyl ether, described above; "mixed" m. p. 123° (Found: Cl, 16·2%).

5-Chloro-3-methoxydimethylaniline.—5-Chloro-3-methoxyaniline (6 g.), methyl alcohol (12 c.c.), and methyl sulphate (11 c.c.) were heated together in a sealed tube at 165° for 6 hours. (At a higher temperature charring takes place.) The mixture was diluted with water (200 c.c.), made faintly alkaline, and steam-distilled. The oil that passed over was treated with acetic anhydride and again

steam-distilled, 5-*chloro-3-methoxydimethylaniline* being thus obtained as a colourless oil (Found: Cl, 19·2. $C_9H_{12}ONCl$ requires Cl, 19·1%) readily soluble in dilute acids.

Nitrosation. A solution of 5-chloro-3-methoxydimethylaniline (2 g.) in concentrated hydrochloric acid (3 c.c.) was diluted with water (30 c.c.), cooled to 0°, and treated gradually with sodium nitrite (1·5 g. in water, 10 c.c.); a yellow hydrochloride separated. 5-*Chloro-4-nitroso-3-methoxydimethylaniline* was liberated from this. After being washed with ether, it crystallised from methyl alcohol in green needles, decomp. 155° (Found: Cl, 16·4. $C_9H_{11}O_2N_2Cl$ requires Cl, 16·6%). It is insoluble in light petroleum, sparingly soluble in ether and carbon tetrachloride, but more readily soluble in chloroform, benzene, and acetone; the solutions are green. It does not give the Liebermann nitrosoamine reaction, develops a deep cherry-red colour in concentrated sulphuric acid, and is completely decomposed on prolonged boiling with 10% aqueous potassium hydroxide, methylamine being evolved.

TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, December 17th*, 1927.]

XLVI.—*The Comparative Reactivities of Some Chloro-, Bromo-, and Iodo nitrobenzenes.*

By ALBERT BREWIN and EUSTACE EBENEZER TURNER.

IN an attempt to determine the relative degrees to which chlorine, bromine, and iodine atoms are activated by nitro-groups, present in the same aromatic nucleus, we chose piperidine as reagent for reasons already stated (Le Fèvre and Turner, J., 1927, 1113), and first tried to compare the reactivities of different halogenonitro-compounds by allowing them to compete, two at a time, for piperidine in benzene solution. The results, however, did not lend themselves to simple interpretation, and we therefore made quantitative measurements of the reactivity of individual halogeno-nitro-compounds towards piperidine. The reactivity of *p*-chloronitrobenzene, the least reactive compound used, being expressed by unity, the compounds mentioned below have reactivities for this one reagent, and under the present definite conditions, represented by the attached figures:

o-Chloronitrobenzene	36·3	1-Chloro-2 : 4-dinitrobenzene	56·9
o-Bromonitrobenzene	43·5	1-Bromo-2 : 4-dinitrobenzene	56·4
o-Iodonitrobenzene	17·9	1-Iodo-2 : 4-dinitrobenzene ...	34·4
p-Bromonitrobenzene	2·38	4-Chloro-3-nitrobenzonitrile	56·1
p-Iodonitrobenzene	2·24	4-Bromo-3-nitrobenzonitrile	55·1
2 : 5-Dichloronitrobenzene	55·9		
2 : 5-Dibromonitrobenzene	56·0		

The results show that, whereas *o*-chloronitrobenzene is about 36 times as reactive as the corresponding *p*-compound, the *o*-bromo- and *o*-iodo-compounds are respectively only 18 and 8 times as reactive as the *p*-analogues. They also seem to show that iodine is incapable of activation to the extent possible with chlorine and bromine.

Competitive Experiments.—In the first series of experiments, a pair of halogenonitro-compounds (1 mol. of each) was allowed to react with piperidine in 100 c.c. of benzene, at 15° for 60 hours (dinitro-compounds) or in the boiling solvent for 8 hours (*o*-nitro-compounds). The results are in Tables I and II.

TABLE I.

w = g. of silver halide from 50 c.c. of solution; v = c.c. of $0\cdot1038N$-$AgNO_3$ required by 50 c.c. of solution; r = molecular ratio of piperidine salts in the mixture.

Pair of 1-halogeno-2 : 4-dinitrobenzenes.	w.	v.	r.
Cl, Br	0·1860	11·23	Cl : Br = 1·75 : 1
Br, I	0·1661	7·26	Br : I = 1 : 2·22
I, Cl	0·1115	6·95	I : Cl = 1 : 6·83

In each of these cases the mixed piperidine salts, made up to 1 litre with water, were analysed in the usual manner, but in experiments 2 and 3, where iodine ions were present, more accurate results were obtained by adding excess of silver nitrate and titrating the final excess with ammonium thiocyanate.

TABLE II.

w' = g. of mixed piperidine hydrohalides; w = g. of mixed silver halides from 50 c.c. of solution; r = molecular ratio of piperidine salts in the mixture.

Pair of 1-halogeno-2-nitrobenzenes.	w'.	w.	r.
Cl, Br	2·3488	0·1344	Cl : Br = 0·6 : 1
Br, I	2·0240	0·1130	Br : I = 1·5 : 1
I, Cl	0·9033	0·0523	I : Cl = 1 : 5·4

In these experiments the mixture of piperidine salts was collected in a Gooch crucible, washed with benzene, dried to constant weight at 100°, and then analysed gravimetrically.

From the first two experiments in Table I and in Table II iodine would be expected to be a little more reactive than chlorine; it appears from the third experiment in each table to be considerably less so.

Direct Method of Measurement.—The halogenonitro-compound (0·02468 g.-mol., equiv. to 5 g. of 1-chloro-2 : 4-dinitrobenzene) was allowed to react for 8 hours in boiling benzene solution (50 c.c.) with piperidine (1 mol.); the precipitated piperidine salt was then

collected in a Gooch crucible and dried at 100°. The results are in Table III.

TABLE III.

	Substance.	Percentage reaction. Series 1.	Series 2.	Mean.	Ratio (Cl = 1).
ortho-	$C_6H_4Cl\cdot NO_2$	59·7	60·1	59·9	1
	$C_6H_4Br\cdot NO_2$	71·6	72·0	71·8	1·20
	$C_6H_4I\cdot NO_2$	29·6	29·4	29·5	0·49
para-	$C_6H_4Cl\cdot NO_2$	1·6	1·7	1·65	1
	$C_6H_4Br\cdot NO_2$	3·9	3·85	3·93	2·38
	$C_6H_4I\cdot NO_2$	3·9	3·5	3·7	2·22
1 : 2 : 4-	$C_6H_3Cl(NO_2)_2$	95·8	92·2	94·0	1
	$C_6H_3Br(NO_2)_2$	94·8	91·2	93·0	0·99
	$C_6H_3I(NO_2)_2$	56·8	56·5	56·7	0·60
1 : 2 : 4-	$C_6H_3Cl(NO_2)\cdot CN$	92·85	92·1	92·5	1
	$C_6H_3Br(NO_2)\cdot CN$	90·5	91·4	91·0	0·98
1 : 2 : 5-	$C_6H_3(NO_2)Cl_2$	92·9	91·7	92·3	1
	$C_6H_3(NO_2)Br_2$	93·1	91·7	92·4	1
1 : 4-	$C_6H_4Cl\cdot NO_2$	1·65		1·65	1
1 : 3 : 4-	$C_6H_3(NO_2)Cl_2$	3·9	3·9	3·9	2·36

One of us is indebted to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

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XLVII.—*The Mechanism of Activation of Halogen Atoms by a Nitro-group Present in the Same Aromatic Nucleus.*

By ALBERT BREWIN and EUSTACE EBENEZER TURNER.

As a result of some experiments on the relative reactivities of various halogenonitro-compounds (preceding paper), we have been led to consider afresh the general problem of reactivity among such compounds.

Different reagents give very different comparative reactivities for a series of halogenonitro-compounds. Some reagents appear to act only in so far as they are ionised. For instance, Lulofs (*Rec. trav. chim.*, 1901, **20**, 292) showed that the rate of interaction of 1-bromo-2 : 4-dinitrobenzene and sodium ethoxide in alcoholic solution was decreased either by increasing the concentration or by adding sodium bromide or sodium acetate (compare also Segaller, J., 1913, **103**, 1154; Shroder and Acree, J., 1914, **105**, 2582; Baudet, *Rec. trav. chim.*, 1924, **43**, 758). In other cases, it is not definitely ascertainable whether the reactions are ionic or not.

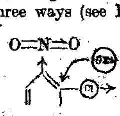
The nitro-group is the only group which in the absence of other

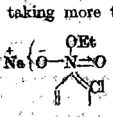
groups is known to cause really pronounced activation of halogen atoms. It is, therefore, not only because the nitro-group is a meta-directing group that it exerts so powerful an activating influence. That is, it is not the dipolar structure of the nitro-group that produces the activation, since the sulphone, carboxyl, and sulphoxyl groups produce only feeble activating effects by themselves.

It seems probable, therefore, that the activating effect of the nitro-group depends on the presence of the nitroso-group, O:N, containing apolar oxygen. Moreover, it is known that the nitroso-group (although it is ortho-para directing) exerts a very powerful influence by itself on substituents in the para-position. For example, *p*-nitrosodimethylaniline reacts with alkali to give *p*-nitrosophenol under conditions which leave *p*-nitrodimethylaniline unchanged, and a second nitro-group is necessary before the dimethylamino-group is readily replaced by hydroxyl (2 : 4-dinitrodimethylaniline). Similarly, as Fischer and Hepp (*Ber.*, 1887, **20**, 2475; 1888, **21**, 684) have shown, *p*-nitrosophenol reacts even at 100° with ammonium acetate, ammonium carbonate, and ammonium chloride to give *p*-nitrosoaniline. *p*-Nitrophenol, on the other hand, is unaffected even by piperidine at the same temperature (Le Fèvre and Turner, J., 1927, 1113).

On first considering the matter it appeared to us that reactions involving alkali alkyloxides were of the direct interaction type, whereas those involving bases were indirect, additive compounds being formed intermediately. On the other hand, coloured additive compounds are certainly formed in both cases, and there seems no reason to assume that the additive compounds are unessential in one case and essential in the other. It is conceivable that the formation of additive compounds could actually hinder the main reaction (compare the Friedel–Crafts reaction, as studied by Olivier, *Rec. trav. chim.*, 1926, **45**, 817).

In the typical case of *o*-chloronitrobenzene, according to modern theories, the nitro-group seeks to acquire more than its due half-share in the pair of N–C_α co-valency electrons, and does so at the expense of C_β to which chlorine is attached. This carbon atom therefore tends to gain control over an electron and it can do this in one of three ways (see I): (1) by taking more than its due

(I.) 



(II.)

half-share of the C_β–Cl pair, (2) by tentative borrowing from the $C_\beta C_\gamma$ electrons, or (3) by attaching an electron outside the mole-

cule. Now chlorine cannot be regarded as willing to relinquish its share in an electron with which, as we know, it separates from C_β as a result of the completion of the process under discussion. Process (2) must occur to some extent, otherwise *p*-chloronitrobenzene would not be reactive, but (3) is also probable in many cases. For instance, when the reagent is sodium ethoxide, C_β endeavours to acquire an electron from the negative ethoxyl ion, and, at this moment, chlorine, which has a great tendency to become an ion, takes entire charge of the original C_β–Cl pair. As a result, the already adjacent ethoxyl group becomes attached to C_β.

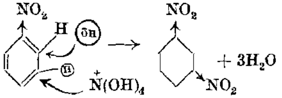
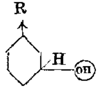
A similar process may be assumed to occur in reactions involving bases, the basic residue being substituted for the ethoxyl group. It is also clear that the above process of electron drift produces an alternating effect, so that *m*-chloronitrobenzene is not reactive.

On the other hand, this theory, without modification, requires that other meta-directing groups should cause ortho-para activation, and that ortho-para-directing groups, at any rate in so far as they are definitely polar (*e.g.*, $\bar{O}$ in phenoxides), should cause meta activation. Since these activations are only observed to a slight extent, we must adopt the view, originally due to Kenner and others, that the nitro-group is activating because it forms additive compounds. Now the additive compound with sodium ethoxide would probably be (II), in which the ethoxyl radical would be expected to undergo ortho-para wandering either of the inter- or of the intra-molecular type (compare Ingold, J., 1927, 1245). It will naturally be attracted to C_β for reasons already given. Elimination of chlorine as the ion is a necessary subsequent process for the attainment of electrical neutrality (separation of solid sodium chloride, frequently insoluble in the reaction mixture, etc.), and it should be noted that the additive compound is formed without destruction of the positive charge on the nitrogen atom, and with the actual attachment of a negative charge to the originally neutral oxygen atom.

In a similar way, a base NHR_2 would form the intermediate additive compound in which H replaces Na and NR_2 replaces OEt. Activation of substituents (*e.g.*, nitro-groups) other than halogen atoms can be discussed in the same manner.

On similar lines, the nitration of nitrobenzene (or other compound undergoing *m*-substitution) is capable of explanation. In the case of nitrobenzene, C_β can acquire control of one of the electrons of the negative hydroxyl ion present in the nitrating solution (see below). The simultaneous electron shift from the $C_\gamma C_\beta$ bond to C_γ causes attraction of the positive NO_2 ion, and

there is formed the Obermiller type of additive compound (III), which then changes to *m*-dinitrobenzene owing to the driving force

(III.)   (IV.)

of water elimination. The preliminary addition of the elements of the reagent to the nitro-group is here unnecessary, and it is known that nitrobenzene nitrates less rapidly than benzoic acid, showing that the unique characteristics of the nitro-group as regards activating effects do not come into play in this case.

Although, as Wieland and Sakellarios (*Ber.*, 1920, **53**, 201) have shown, nitric acid combines with ethylene to give β-nitroethyl alcohol, that is, it reacts as if it had separated into OH^- and NO_2^+ ions, objection may be taken to the assumption usually made that aromatic nitration involves these ions. This difficulty can be surmounted if it be assumed that orthonitric acid is the actual nitrating agent, and that this compound is represented by $[\overset{+}{N}(OH)_4]\overset{-}{O}H$. This substance could supply hydroxyl ions, and instead of a nitro-group one must assume addition of $N(OH)_4$, which is equivalent in effect to that group.

If the above theory accounts for the *m*-nitration of nitrobenzene, etc., then with an ortho-para directing group it will be C_γ which will attract an OH^- ion, giving (IV). The $[\overset{+}{N}(OH)_4]$ ion can then add either to C_β or to C_δ, and the proportions of these will depend particularly on the bulk of R; for instance, one would expect *tert.*-butylbenzene to nitrate mainly in the para-position, as it does. Previous theories, not involving the prior attachment of hydroxyl in the meta-position, do not explain so simply why a bulky group has a low ortho-para directive ratio.

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XLVIII.—*The Nitration of Benzaldoxime and Some of its Derivatives.*

By OSCAR L. BRADY and BRIAN E. M. MILLER.

THE orienting influence of the aldoximino-group has not been investigated, probably on account of its instability. With due precautions, however, it is possible to nitrate benzaldoxime, but

the yield of nitro-derivative is poor owing to the difficulty of suppressing hydrolysis and oxidation leading to the formation of acid.

Vorländer (*Ber.*, 1919, **52**, 262) suggested that a positive pole attached to the benzene nucleus is meta-orienting and it has been shown that the introduction of successive saturated carbon atoms between a positive pole and the nucleus diminishes somewhat the meta-orienting effect (Flürscheim and Holmes, J., 1926, 1562; Ing and Robinson, *ibid.*, p. 1655; Goss, Ingold, and Wilson, *ibid.*, p. 2440; Goss, Hanhart, and Ingold, J., 1927, 250). Ingold (*Ann. Reports*, 1926, **23**, 131) suggests that the introduction of unsaturated carbon atoms between a positive pole and the benzene nucleus should cause a more rapid damping of the meta-orienting influence, but this is not borne out in the case of benzaldoxime and *N*-methylbenzaldoxime, which, in the presence of concentrated sulphuric acid, must be regarded as $CHPh{:}\overset{+}{N}{<}^{H}_{OH}$ and $CHPh{:}\overset{+}{N}{<}^{Me}_{OH}$ respectively. Both these compounds on nitration gave *m*-nitro-derivatives; the yields were poor and no indication of the production of *o*- and *p*-derivatives was obtained.

Since *O*-methylbenzaldoxime seems quite devoid of basic properties (Brady, Dunn, and Goldstein, J., 1926, 2388), its nitration is of particular interest. Although a monosubstituted benzene derivative, it resists the action of nitrating agents in an extraordinary manner: treatment with a mixture of fuming sulphuric acid and fuming nitric acid at room temperature gave about 10% of *O*-methyl-*m*-nitrobenzaldoxime, but a large amount of *O*-methylbenzaldoxime was recovered unchanged, and even after warming with the nitrating acid much *O*-methylbenzaldoxime was unacted upon. This abnormal behaviour is in line with the general unreactivity of *O*-methylbenzaldoxime (*e.g.*, its resistance to hydrolysis by acids or alkalis and its non-basic properties) and suggests that the $-CH{:}N{\cdot}OMe$ group in conjunction with the benzene ring represents a system in which free affinity is reduced to a minimum. This may be sufficient to explain why the substitution that occurs is in the meta-position.

When other strongly directive groups are present, the orienting effect of the aldoximino-group is not apparent; *e.g.*, when *p*-methoxy-, 3 : 4-methylenedioxy-, and 3-methoxy-4-hydroxy-benzaldoximes are nitrated, the nitro-group enters in the 3-, 6-, and 5-positions, respectively, as in the case of the corresponding aldehydes. The *O*-methyl ethers of *p*-methoxy- and 3 : 4-methylenedioxy-benzaldoximes are readily nitrated, the nitro-group entering in the 3- and 6-positions, respectively.

Experimental.

α-Benzaldoxime.—The nitrating acid was prepared by adding 120 g. of fuming sulphuric acid (10% SO_3) to 12 c.c. of nitric acid (*d* 1·42), through which a current of air had been passed to remove nitrous acid as completely as possible.

α-Benzaldoxime (12 g.) was added with stirring to the above nitrating acid (54 g.), cooled in ice, at such a rate that the temperature did not rise above 0°; after a short time, the mixture was poured on ice. The red pasty mass thus obtained solidified after being washed with water. It was ground with 2*N*-sodium hydroxide, and to the yellow solution, filtered after dilution, an excess of a saturated solution of ammonium chloride was added. The precipitated oxime was collected, washed, dried, and crystallised from benzene–light petroleum, 4·5 g. (30% of the calculated amount) of *m*-nitrobenzaldoxime (m. p. 120°), identified by comparison with an authentic specimen, being obtained.

In a second experiment the precipitated oxime was collected and that dissolved in the mother-liquor was recovered by extraction with chloroform. The whole of the oxime so obtained was crystallised from benzene–light petroleum: the greater part of the *m*-nitrobenzaldoxime having thus been removed, the mother-liquor was examined for *o*- or *p*-derivative. It was evaporated to dryness, and the residue hydrolysed by heating under reflux with concentrated hydrochloric acid for 3 hours. After cooling, dilution, extraction with chloroform, and removal of the solvent 0·5 g. of aldehyde was obtained; this was converted into the phenylhydrazone, fractional crystallisation of which gave no indication of the presence of the *o*- or *p*-nitro-compound, the fractions melting at 120—121° and not depressing the melting point of *m*-nitrobenzaldehydephenylhydrazone (m. p. 122°) (compare Brady and Harris, J., 1923, **123**, 485).

α-O-Methylbenzaldoxime.—α-*O*-Methylbenzaldoxime (5 g.), dissolved in ice-cold concentrated sulphuric acid (10 g.), was added at 0° to 20 g. of a nitrating acid made by adding 85 g. of concentrated sulphuric acid to 10 c.c. of nitric acid (*d* 1·5). When the mixture had attained room temperature, a portion was poured on ice; the oil obtained was largely *O*-methylbenzaldoxime; other portions were warmed to various temperatures not exceeding 80°, but in no case was there any indication of nitration.

O-Methylbenzaldoxime (2 c.c.) was added cautiously to fuming nitric acid (5 c.c.) at room temperature: when about half had been added, a brisk effervescence occurred. At the end of the reaction the solution was poured on ice, the odour of benzaldehyde

being then very perceptible. The benzaldehyde was extracted with ether, isolated in the form of the sodium bisulphite compound, regenerated, and identified by conversion into the semicarbazone.

O-Methylbenzaldoxime (5 g.) was added slowly to 10 c.c. of a nitrating acid (made by adding 78 g. of fuming sulphuric acid to 13·3 c.c. of fuming nitric acid), cooled in running water; considerable frothing occurred. After remaining at room temperature for 1½ hours, the mixture was poured on ice and then extracted with chloroform. The chloroform solution was shaken with 2*N*-sodium carbonate, and the reddish-yellow aqueous layer obtained, on being acidified and extracted with ether, gave about 0·1 g. of impure *m*-nitrobenzoic acid. The chloroform solution was then shaken with sodium bisulphite solution; no solid separated and the bisulphite solution, when distilled with sodium carbonate, gave no aldehyde. The chloroform solution was dried over anhydrous sodium sulphate, most of the solvent removed, and the residue fractionated, 1·1 g. of unchanged *O*-methylbenzaldoxime being collected at 180—200°. An ethereal solution of the residue in the flask was filtered from a small amount of tar and evaporated; the residual oil, which still had a strong odour of *O*-methylbenzaldoxime, was seeded with a minute trace of *O*-methyl-*m*-nitrobenzaldoxime and scratched vigorously, crystals beginning to separate after some minutes. The mixture was kept in a desiccator for 4 days and the crystals were then collected, pressed on a tile, and crystallised from dilute alcohol; the *O*-methyl-*m*-nitrobenzaldoxime (0·5 g.) obtained was identified in the usual way. The residual oil, probably mainly *O*-methylbenzaldoxime, weighed 0·76 g., and therefore about 50% of the *O*-ether was accounted for.

N-*Methylbenzaldoxime*.—Finely powdered *N*-methylbenzaldoxime (5 g.) was sprinkled cautiously with stirring into 7·5 c.c. of a nitrating acid (made from 78 g. of fuming sulphuric acid and 13·3 c.c. of fuming nitric acid and freed from nitrous acid by addition of urea), the temperature being kept below 5°. The mixture was poured on ice and extracted with chloroform several times and the combined extracts were dried over anhydrous sodium sulphate and saturated with hydrogen chloride. The precipitated hydrochloride was decomposed with 2*N*-sodium carbonate, the solid collected, and the solution extracted with chloroform. The solid (m. p. 109—110°) together with that obtained by evaporating the chloroform weighed 0·77 g. and after crystallisation from benzene gave *N*-methyl-*m*-nitrobenzaldoxime, m. p. 117°.

The mother-liquor from the crystallisation was evaporated, the residue hydrolysed by boiling with concentrated hydrochloric acid,

and, after dilution, the aldehyde was extracted with ether and converted into the phenylhydrazone, which was fractionally crystallised; no indication of the presence of *o*- or *p*-nitro-derivative was obtained.

The filtrate from the hydrochloride precipitate was washed with sodium carbonate solution, dried, and evaporated and the residual oil was converted into a semicarbazone, 2·5 g., m. p. 209—210°, being obtained. This was apparently a mixture of the semicarbazones of benzaldehyde and *m*-nitrobenzaldehyde, repeated crystallisations from alcohol giving a fairly pure specimen of the latter.

In another experiment the chloroform solution, instead of being treated with hydrogen chloride, was thoroughly washed with water and distilled in a current of steam. The residual liquid, on extraction with chloroform, gave 1·14 g. of a mixture of *N*-methyl-*m*-nitrobenzaldoxime and *m*-nitrobenzaldehyde (m. p. 72—74°), from which 0·45 g. of *N*-methyl-*m*-nitrobenzaldoxime was isolated after several crystallisations from benzene. The chloroform layer in the distillate, after evaporating, gave 0·53 g. of an uncrystallisable oil with a strong odour of benzaldehyde.

A solution of *N*-methylbenzaldoxime in acetic acid, on treatment with nitric acid, slowly turned green and a copious evolution of gas occurred owing to oxidation; addition of water precipitated benzaldehyde.

α-p-Methoxybenzaldoxime.—The oxime (1 g.), dissolved in concentrated sulphuric acid (4 c.c.), was added to 2·5 c.c. of a nitrating acid (prepared from concentrated sulphuric acid, 85 g., and 70% nitric acid, 15 c.c.), the temperature being kept below 10°. The mixture was poured on ice and extracted with chloroform and the extract was shaken with *N*-sodium hydroxide to remove oxime. The aqueous layer, on being saturated with carbon dioxide, gave a pale yellow precipitate which, after two crystallisations from benzene, gave 3-nitro-4-methoxybenzaldoxime.

α-O-Methyl-p-methoxybenzaldoxime.—Preliminary experiments showed that when *O*-methyl-*p*-methoxybenzaldoxime was nitrated, a mixture of mono- and di-nitro-compounds was formed which was difficult to separate. The conditions were therefore chosen to favour the production of one or other of the compounds.

O-Methyl-*p*-methoxybenzaldoxime (2·6 g.), dissolved in concentrated sulphuric acid (15 c.c.), was added to 10 c.c. of a nitrating acid of the composition used in the case of *O*-methylbenzaldoxime, the temperature being kept below 30°. The solid obtained on pouring the mixture on ice was freed with difficulty from mononitro-compound by crystallising it four times from acetone and water; *O-methyl-3 : 5-dinitro-4-methoxybenzaldoxime* was then

obtained in colourless needles, m. p. 129° (Found: N, 16·9. $C_9H_9O_6N_3$ requires N, 16·5%).

O-Methyl-*p*-methoxybenzaldoxime (0·5 g.), dissolved in concentrated sulphuric acid (5 c.c.), was added to 3 c.c. of a nitrating acid (prepared from 90 g. of concentrated sulphuric acid and 5·2 c.c. of 70% nitric acid), the mixture being cooled in running water. On pouring it on ice, 0·54 g. of crude product was obtained, m. p. 103—104°. Three crystallisations from alcohol gave slightly impure *O*-methyl-3-nitro-4-methoxybenzaldoxime, m. p. 116—117°, which, when mixed with a pure specimen (m. p. 120°), melted at 118—118·5°.

α-3 : 4-*Methylenedioxybenzaldoxime*.—A solution of the oxime (2 g.) in acetic anhydride (10 c.c.) was added at 0° to 10 c.c. of a nitrating mixture prepared by adding nitric acid (3 c.c., *d* 1·5) to acetic anhydride (45 c.c.). After being kept for a short time on ice, the reaction mixture was poured into water. The orange oil obtained (2·4 g.), consisting of a mixture of oxime and acetyl derivative, solidified when scratched. It was then finely powdered and suspended in cold 2*N*-sodium hydroxide, dissolving after 12 hours. Saturation of the solution with carbon dioxide precipitated 6-nitro-3 : 4-methylenedioxybenzaldoxime (1·1 g.), which was obtained pure after crystallisation from benzene.

α-O-*Methyl*-3 : 4-*methylenedioxybenzaldoxime*.—A solution of *O*-methyl-3 : 4-methylenedioxybenzaldoxime (1 g.) in glacial acetic acid (10 c.c.) was added to a 5% solution of fuming nitric acid in acetic acid (13 c.c.). No action occurred, but on heating on the water-bath for 5 minutes the solution turned brown; after cooling, it was poured on ice, 1·29 g. of a pale yellow precipitate, m. p. 143°, being obtained. One crystallisation from dilute alcohol gave 0·82 g. of pure *O*-methyl-6-nitro-3 : 4-methylenedioxybenzaldoxime, m. p. 147°.

α-3-*Methoxy*-4-*hydroxybenzaldoxime*.—The oxime (1 g.) was dissolved in glacial acetic acid (5 c.c.), and a 5% solution of fuming nitric acid in acetic acid (10 c.c.) added. The solution, which became dark, was immediately cooled in running water; 5-nitro-3-methoxy-4-hydroxybenzaldoxime then crystallised in almost quantitative yield. After being washed with a little acetic acid and with water and crystallised from alcohol, it gave the pure compound in excellent yield.

The Ralph Forster Laboratories of Organic Chemistry,
University College, London. [*Received, December 5th*, 1927.]

XLIX.—*The Addition of Bromine to Ethylenic Compounds in Non-hydroxylic Solvents.*

By David Matthew Williams and Thomas Campbell James.

It is generally stated that the addition of halogens to unsaturated ethylenic compounds in dilute solution takes place in accordance with the bimolecular law (Herz and Mylius, *Ber.*, 1906, **39**, 3816; Hofmann and Kirmreuther, *Ber.*, 1909, **42**, 4481; Barrett and Lapworth, P., 1907, **23**, 18; Bauer and Moser, *Ber.*, 1907, **40**, 918; Sudborough and Thomas, J., 1910, **97**, 715, 2450). In aqueous solution, the reaction takes place very rapidly, whilst in non-aqueous solvents the rate of addition is said to vary according to (i) the position of the ethylenic linkage, (ii) the presence of certain substituent groups, (iii) the solvent, and (iv) the presence of catalysts and especially of light. Published results indicate that the rate of reaction is extremely sensitive to slight variation of these conditions; *e.g.*, Sudborough and Thomas's values for the velocity coefficient for cinnamic acid and bromine vary from $0{\cdot}9 \times 10^{-4}$ to $2{\cdot}6 \times 10^{-4}$ in series of experiments carried out under apparently identical conditions.

We have examined the addition of bromine to a number of unsaturated acids and their derivatives in dry chloroform and carbon tetrachloride in the dark, and although these results are of a preliminary nature, we have reached the following general conclusions:

1. The substances examined can be divided into three classes: (*a*) Those to which bromine is added with considerable rapidity, the addition being accompanied by substitution and the formation of hydrogen bromide: the bimolecular velocity coefficient steadily decreases as the reaction proceeds. This class includes such diversely constituted substances as oleic and elaidic acids, *cis*- and *trans*-*o*-methoxycinnamic acids, acids containing conjugated double bonds such as cinnamylideneacetic acid and its methyl ester, phenylstyrylacrylic acid and furfurylacrylic acid. (*b*) Those to which bromine adds on slowly but with a measurable and increasing velocity, exhibiting a preliminary inhibition period. This class includes cinnamic acid and its methyl ester, crotonic acid, and methyl cinnamylidenemalonate. (*c*) Those to which no measurable addition takes place under the conditions investigated. This class includes compounds possessing cyclic structures, *e.g.*, maleic anhydride and coumarin, and also α-phenylcinnamonitrile.

The evidence obtained seems to show that the difference between the classes is not so much a question of degree as of type, and every substance examined fell naturally into one class or other.

2. The position of the double bond, especially in the α-position *to the carboxyl group, and of substituent groups in close proximity* to the double bond (*e.g.*, the nitrile group in α-phenylcinnamonitrile) have an important effect on the rate of addition (compare Sudborough and Thomas, *loc. cit.*, p. 2452), but these are not the deciding factors as is shown by the behaviour of the *o*-methoxycinnamic acids and of the isomeric *p*-acid (Hariharan and Sudborough, *J. Ind. Inst. Sci.*, 1925, **8A**, 193).

3. The rapidity of addition to substances of class (*a*) above, is due to preliminary substitution, with the formation of hydrogen bromide in small amounts. This is borne out by the effect of the addition of quantities of hydrogen bromide to the reacting substances of class (*b*), whereby the rates of addition are much accelerated *and vary with the concentration* of the catalyst. Hydrogen chloride and water produce similar effects to hydrogen bromide, although not of the same degree. In each case, the inhibition period disappears and the reaction becomes bimolecular. Addition to substances of class (*c*) does not occur under the influence of any of the above catalysts.

In general, the reactions were *more* rapid *in chloroform* than *in* carbon tetrachloride.

EXPERIMENTAL.

Purification of Materials.—The solvents (carbon tetrachloride and chloroform) were washed with acid, alkali, and water, then dried for extended periods over calcium chloride, and finally distilled over phosphorus pentoxide. The bromine was shaken with concentrated sulphuric acid, purified by freezing several times until of constant melting point, and then distilled over pure potassium bromide. The acids and their derivatives were recrystallised until of constant melting point and finally dried for long periods in a vacuum.

The method described by Sudborough and Thomas (*loc. cit.*) was followed in all essential details. Equal volumes of *M*/30-solutions of the unsaturated compound and of bromine in the purified solvent were mixed in brown bottles and kept in a thermostat at 13° in a dark room. After definite intervals of time the reaction was stopped by the addition of a definite volume of 0·1*N*-potassium iodide, followed, after shaking, by a definite excess of *N*/30-sodium thiosulphate. After shaking until the iodine had been completely absorbed from the solvent layer, the excess of thiosulphate was estimated by back titration with *N*/30-iodine solution. From these data, calculation gave the amount of unabsorbed bromine remaining in the reaction mixture

In subsequent experiments it was possible, for substances of class (b), to use a single reaction vessel with all-glass, air-tight fittings, from which samples of the reaction mixture were expelled into potassium iodide solution by forcing in dry air. These samples were weighed and analysed as before. Results obtained in this way were in general agreement with those previously obtained but more consistent amongst themselves.

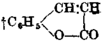
In studying the effects of hydrogen chloride and hydrogen bromide as catalysts, small, definite volumes of saturated solutions of these gases in carbon tetrachloride were added to the reaction mixture, the decrease in the initial concentration of the reactants being thus known. Saturated solutions of hydrogen chloride and hydrogen bromide in carbon tetrachloride at 13° contain 0·42 and 1·80% of the gases, respectively.

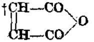
TABLE I.

Temperature 13°, unless otherwise stated.

Substance.	Approx. inhibition period (hours).	Period for 25% change.	k, first value.	k, last value.
Class (*a*).				
**trans-o*-$C_6H_4(OMe)\cdot CH:CH\cdot CO_2H$	—	0·01	1,074	102
†*cis*- ,,	—	0·02	1,578	126
**cis*- ,,	—	0·01	1,824	144
*$C_6H_5\cdot CH:CH\cdot CH:CH\cdot CO_2H$	—	0·01	882	174
†$C_6H_5\cdot CH:CH\cdot CH:CH\cdot CO_2Me$ ...	—	0·02	97·8	5·4
* ,, ...	—	0·01	2,562	420
*$C_6H_5\cdot CH:CH\cdot CH:CPh\cdot CO_2H$	—	0·3	65·4	42·0
*$C_4H_4O\cdot CH:CH\cdot CO_2H$	—	0·01	1,134	162
†Oleic acid	—	0·001	78,000	780
†Elaidic acid	—	0·001	102,000	3840
Class (*b*).				
*$C_6H_5\cdot CH:CH\cdot CO_2H$	12	65	0·078	0·792
† ,, ...	20	156	0·066	0·246
† ,, (at 0°)	20	206	0·039	0·096
† ,, (*at 25·5°*) ...	10	31	0·426	0·702
†$C_6H_5\cdot CH:CH\cdot CO_2Me$	42	280	0·039	0·063
†$CH_3\cdot CH:CH\cdot CO_2H$	18	195	0·063	0·120
†$C_6H_5\cdot CH:CH\cdot CH:C(CO_2Me)_2$	22	117	0·126	0·234

Class (*c*).

† .... 7·0% change in 352 hours.

† .... 5·4% change in 306 hours.

†$C_6H_5\cdot CH:CPh\cdot CN$ .... 5·8% change in 280 hours.

* Indicates reactions in chloroform as solvent.

† Indicates reactions in carbon tetrachloride as solvent.

A constant water content in the solvent was obtained by the introduction of sodium sulphate–decahydrate salt-pair (compare Bury and Roberts, J., 1923, **123**, 2037). If the vapour pressure of the salt-pair be taken as 7·91 mm. at 13° and that of water at 13° as 11·23 mm., the solvent will be 70% saturated with water in the presence of the salt–hydrate pair.

The use of carbon tetrachloride as a solvent was limited, since many of the substances examined were not sufficiently soluble in it. In those cases, chloroform only was used.

The results are shown in the tables, the bimolecular velocity coefficient, $k = 1/t.x/a(a - x)$, being based upon time (t) in hours and concentrations (a and x) in g.-mols. per litre. Two typical results illustrating the variation of k in the addition of bromine to substances of classes (*a*) and (*b*) are afforded respectively by *trans-o*-methoxycinnamic acid in chloroform, in which k fell continuously from 1074 to 102 during 2½ hours, and by cinnamic acid in carbon tetrachloride, in which, after an induction period of some 15—25 hours, k rose from 0·066 at 69 hours to 0·246 at 247 hours.

Table I summarises the results for all the substances used. Table II shows the effects of the three catalysts used.

TABLE II.

Solvent CCl_4.

	Catalyst.	(*a*).	(*b*).	k_1.	k_2.
Cinnamic acid	HBr	0·26	1·25	18·0	16·6
,, ,, ...	,,	0·53	0·37	58·2	72·0
,, ,, ...	,,	1·08	0·16	132	156
,, ,, ...	HCl	1·10	50	0·474	0·510
,, ,, ...	H_2O	—	104	0·168	0·186
Crotonic acid	HBr	0·53	5·2	5·94	0·98
,, ,, ...	H_2O	—	15	1·74	2·46
Methyl cinnamylidenemalonate	HBr	0·53	0·05	384	408
,, ,, ,,	HCl	1·10	2·8	10·8	5·52
,, ,, ,,	H_2O	—	55	0·642	0·588
Methyl cinnamate	,,	—	72	0·210	0·102

Column (*a*) gives the molar ratio of catalyst : bromine; column (*b*) gives the time (in hours) for 25% change; k_1 and k_2 are respectively the first and last values of k (generally up to 80% addition). With water as catalyst the solvent was 70% saturated

Summary and Conclusion.

The results tabulated above indicate that hydrogen bromide a very effective catalyst in the addition reaction between ethylen acids and bromine. Further, they suggest that when an unsaturat acid and bromine are brought into contact, the first reaction th occurs is substitution with the formation of hydrogen bromide; th

in turn catalyses the addition reaction, which then proceeds in general much more rapidly than the substitution reaction.

It is to be noted that the reactions described in this paper have been conducted in the absence of light. There is reason to believe that radiant energy gives rise to reactions of different type.

One of us (D. M. W.) desires to record his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant.

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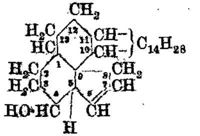
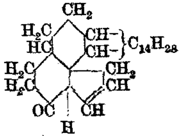
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH. [*Received, December 7th*, 1927.]

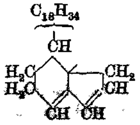
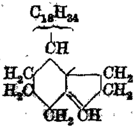
L.—*Studies in the Sterol Group. Part II. The Formation of ψ-Cholestene and Cholestenone by the Dry Distillation of Cholesterol.*

By ISIDOR MORRIS HEILBRON and WILFRED ARCHIBALD SEXTON.

THE effect of heat on cholesterol (I) was first studied by Diels and Linn (*Ber.*, 1908, **41**, 260), who found that it was converted into a mixture of cholestenone (II) and β-cholesterol at 310°, hydrogen being evolved. Their statement that the dehydrogenation is due to the presence of minute quantities of iron or zinc in the cholesterol cannot be substantiated.

(I.)   (II.)

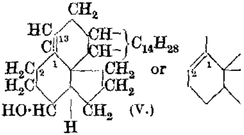
More recently, Fantl (*Monatsh.*, 1926, **47**, 251) converted cholesterol into cholesterilene, to which the structure (III) is ascribed, by distillation with zinc dust under reduced pressure, the reaction being represented as a simple dehydration of the alcohol.

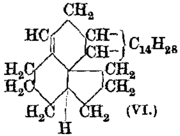
(III.)   (IV.)

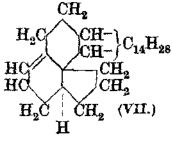
On the other hand, Windaus has shown (*Annalen*, 1927, **453**, 101) that when cholesterol is heated with nickel in absence of hydrogen the saturated ketones cholestanone and coprostanone are produced, a result which he considers may be due to the formation of *allo*-cholesterol (V) prior to the intramolecular rearrangement.

We have now found that the dry distillation of cholesterol at *atmospheric pressure* gives rise to yet another reaction whereby, together with hydrogen, water, and a complex mixture of low-boiling hydrocarbons, cholestenone and ψ-cholestene result. The former compound was isolated and recognised by means of its characteristic semicarbazone, and the identity of the ψ-cholestene was confirmed (*a*) by analysis, (*b*) by the melting point of a mixture with ψ-cholestene prepared by Mauthner's method (*Monatsh.*, 1907, **28**, 1113), (c) by means of its dibromide, and (*d*) through its catalytic hydrogenation to cholestane and ψ-cholestane.

Fischer and Treibs (*Annalen*, 1926, **446**, 241) also have noted th formation of ψ-cholestene and hydrogen from boiling cholestero at a pressure of 300 mm., but they failed to detect cholestenone They conclude that the reaction occurs through the intermediat formation of cholesterilene (III), reduction to ψ-cholestene (IV supposedly occurring through 1 : 4-addition. Although in agree ment with these authors that the latter compound is a direc reduction product of cholesterilene, we are unable to accept thei suggested mechanism for the following reasons. First, recer work by Windaus (*Nachr. Ges. Wiss. Göttingen*, Jan. 1926) point almost inevitably to the conclusion that ψ-cholestene has tl structure (VI) or (VII) and not the structure (IV) originally ascribe


(V.)


(VI.)


(VII.)

to it (see Windaus, *Ber.*, 1919, **52**, 170), which formula indeed can be shown from models, could not possibly give rise to

isomeric saturated hydrocarbons. Secondly, there is distinct evidence that cholesterilene does not contain a conjugated linkage as both Windaus (*Ber.*, 1906, **39**, 2261) and Fantl (*loc. cit.*) have failed to bring about its reduction by means of sodium and amyl alcohol.

We regard the formation of ψ-cholestene as the result of two distinct reactions: (*a*) dehydration of part of the cholesterol to cholesterilene, and (*b*) dehydrogenation of a further part to cholestenone, the hydrogen evolved in the latter reaction being utilised for the hydrogenation of the cholesterilene. Our experiments have led us to the conclusion that (*b*) takes place more readily than (*a*) and this interpretation is in full accord with the results obtained by other investigators. For instance, the failure of Diels and Linn (*loc. cit.*) to observe dehydration was doubtless due to their maximum temperature being considerably lower than ours. Similarly, in the reaction where Windaus employs nickel, a temperature of only 220° was reached, and this again would account for the absence of either ψ-cholestene or its reduction products. A review of the evidence indeed seems to show that the dehydrogenation of the secondary alcohol group is the fundamental reaction which takes place during the decomposition of cholesterol by heat.

It follows from the foregoing that one of the ethenoid linkages in cholesterilene must occupy the same position as in ψ-cholestene, a conclusion in complete agreement with the observed simultaneous production of cholestane and ψ-cholestane by its catalytic hydrogenation (Windaus and Seng, *Z. physiol. Chem.*, 1921, **117**, 158). The formation of the latter hydrocarbons is inexplicable on the assumption that (III) represents the true position of the ethenoid linkages in cholesterilene.

EXPERIMENTAL.

Cholesterol (200 g.) obtained from cod-liver oil, crystallised from ethyl acetate until the melting point was constant at 148·5°, and dried by prolonged heating in a steam-oven, was distilled in 50 g lots, in a slow current of carbon dioxide, from a Jena glass flask fitted with a Liebig condenser through which water was run during the preliminary stages of the distillation. A second distillation flask served as receiver, the side arm of which was connected with U-tubes, surrounded by ice and salt, for collection of the highly volatile, low-boiling products; the gaseous portion, after passing through wash-bottles containing chloroform, was collected over alkali. The cholesterol was gently heated over a free flame and soon after it had melted a copious evolution of gas commenced. When the temperature had risen somewhat, the liquid began to distil, water and light oil passing over first, followed by a yellow

oil the colour and viscosity of which gradually increased until only red, syrup-like drops distilled. The distillation was stopped at this point and the reddish-yellow distillate (176 g.), which darkened rapidly on exposure to air, was taken up in ether, dried, and fractionally distilled, four fractions being collected: (*a*) 60—100°/atm. press. (3 g.), (*b*) 100—200°/atm. press. (12 g.), (*c*) 140—240°/13 mm. (21 g.), and (*d*) 240—310°/13 mm. (121 g.). The volatile liquid which had condensed in the U-tubes (4 g.) and fraction (*a*) were united and fractionally distilled, but a constant-boiling portion could be obtained neither from them nor from fractions (*b*) and (*c*). These products are probably of the same complex nature as the compounds obtained by Fantl (*loc. cit.*) and by Steinkopf on heating cholesterol with kieselguhr (*J. pr. Chem.*, 1919, **100**, 65).

ψ-Cholestene. Fraction (*d*), which constituted the main portion, was dissolved in warm acetone, and the solution left for 2 days in the ice-chest; a crystalline solid (37 g.), m. p. 60—65°, had then separated. Repeated crystallisation of this from ether–alcohol gave colourless needles, m. p. 78°, which did not depress the m. p of ψ-cholestene prepared by Mauthner's method (*loc. cit.*) (Found C, 87·7; H, 12·2. Calc. for $C_{27}H_{46}$: C, 87·6; H, 12·4%). The substance was further characterised by the preparation of it dibromide, needles, m. p. 116° (Mauthner, *loc. cit.*, gives 116—117°), and also by the isolation of both cholestane and ψ-cholestan following its catalytic hydrogenation. This was carried out in dr ether at room temperature in the presence of palladium-black f(50 hours, the pressure varying from 1 to 1½ atmospheres; fro 3·5 g. of the initial material, 1·6 g. of pure cholestane, m. p. 80 were obtained together with 1·0 g. of ψ-cholestane, m. p. 70—71 These two substances gave no depression of m. p. in admixtu with cholestane and ψ-cholestane prepared from cholestene a cholesterilene, respectively.

The specific rotations of ψ-cholestene obtained from three sep ate distillations of cholesterol were determined in chlorofo solution: $[\alpha]_D = +57{\cdot}5°$ ($c = 2{\cdot}482$), $+57{\cdot}12°$ ($c = 3{\cdot}176$), a $+58{\cdot}58°$ ($c = 2{\cdot}835$). Fischer and Treibs (private communicati found $[\alpha]_D = 43{\cdot}30°$ for the ψ-cholestene obtained by them (comp Heilbron, Morton, and Sexton, this vol., p. 47).

Cholestenone. After the separation of the ψ-cholestene, acetone filtrate was concentrated, but no further crystalline s stance could be isolated. The whole of the acetone was remo and the residual oil was dissolved in alcohol and treated t excess of semicarbazide acetate. After 2 days the copious cipitate (62 g.) was filtered off, dried, and crystallised from alco

the pure semicarbazone (m. p. 234°) separated in gelatinous form but gradually became crystalline. Cholestenone semicarbazone prepared by the method of Diels and Abderhalden (*Ber.*, 1904, **37** 3101) melted at 234° and the m. p. of a mixture of the two substances showed no depression.

After removal of the semicarbazone, the remaining solution was precipitated with water and the oil was extracted with ether and dried. The dark red oil (30 g.) was fractionally distilled in a vacuum. The fractions were yellow, rapidly darkened on exposure to air, and failed to yield either solid material or bromo-derivatives.

We desire to express our thanks to Mr. W. Doran, M.Sc., for his help in this work and also to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of us (W. A. S.).

THE UNIVERSITY, LIVERPOOL. [*Received, September 16th*, 1927.]

LI.—*The Chlorination of Anilides. Part II. The Decomposition of* N-*Chloroacetanilide by Heat.*

By ALAN EDWIN BRADFIELD.

IN any circumstances which are favourable to the initial production of a trace of chlorine, *N*-chloroacetanilide readily undergoes a two-stage transformation involving intermediate production of chlorine and yields *C*-chloroacetanilides (Orton, *Rep. Brit. Assoc.*, 1910, 85); consequently, it seemed probable that the well-known and profound decomposition of the substance above its melting point followed the same course. Porter and Wilbur's recent statement (*J. Amer. Chem. Soc.*, 1927, **49**, 2145) that when *N*-chloroacetanilide is heated at 100° it undergoes a *one-stage* rearrangement, yielding "almost exclusively" *p*-chloroacetanilide, was therefore surprising.

Observations in these laboratories show that when slowly heated in an air-jacketed melting-point apparatus of the Beckmann type *N*-chloroacetanilide melts at 87—88° to a golden liquid with a slight surface scum. If the bath temperature be maintained stationary at 100°, no apparent change takes place for 30 minutes, but the temperature of the molten chloroamide then slowly rises to 110°, and a violent reaction starts, during which the temperature momentarily rises to above 200°. Considerable darkening takes place, and, on cooling, the contents of the tube set to a mass of purple crystals. When a similar reaction takes place in a sealed tube, acid vapours are evolved on opening and the product, which melts indefinitely

between 50° and 150° (Product I), has the peculiar quinone-like odour associated with the products of chlorination of acetanilide. When the sealed tubes are heated in a boiling water-bath (following Porter and Wilbur, *loc. cit.*) the rise of temperature is probably to some extent prevented (the tubes frequently burst), but the product, although lighter in colour, is of approximately the same composition (Product II). The anilides present in each product were separated as pure substances of correct melting point by methods previously recorded (Orton and W. Jones, J., 1909, **95**, 1056; Orton and Bradfield, J., 1927, 986).

	Product I. From 20 g. of *N*-chloro-acetanilide in air-bath at 100°.		Product II. From 4 g. of *N*-chloro-acetanilide in water-bath at 100°.	
Recovered anilides :	g.	%.	g.	%.
o-Chloroacetanilide	3·65	18·2	0·66	16·5
p-Chloroacetanilide	8·19	41·0	2·03	50·7
2 : 4-Dichloroacetanilide	1·40	7·0	0·16	4·0
Acetanilide..................	1·26	6·3	—	—
Total	14·5	72·5	2·85	71·2

The formation of 2 : 4-dichloroacetanilide indicates that, contrary to the opinion of Porter and Wilbur, chlorine appears during the reaction, as in aqueous-acetic acid solutions.

In view of the discrepancy, the following details are appended.

By titration (which indicates impurity with an accuracy of 2 parts in 1000 parts) the chlorine content of an *average* specimen of *N*-chloroacetanilide (Chattaway and Orton, J., 1899, **75**, 1046; 1901, **79**, 274) is *ca.* 20·8% (Calc. : Cl, 20·93%).* Such material does not differ in behaviour from the most carefully purified substance (Found : Cl, 20·95%). The sealed tubes (made from soft glass, 1 cm. internal diameter), which were cleaned with chromic acid, washed with water, and dried with a current of warm air, were filled to a depth of 7·5 cm. by a charge of 3 g. of *N*-chloroacetanilide, and were sealed, with precautions to avoid the entry of flame gases, at 18—20 cm. from the rounded end. The action of ultra-violet light has not been examined in these laboratories.

The author wishes to express his thanks to Professor K. J. P. Orton, F.R.S., for much helpful advice and criticism.

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BANGOR. [*Received, December 29th*, 1927.]

* The melting point of *N*-chloroacetanilide depends on the rate of heating. The highest value observed in these laboratories is 90—90·5° with rapid heating.

LII.—*Syntheses in the Phenazine Series.*

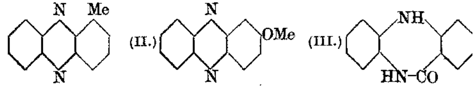
By Hamilton McCombie, Harold Archibald Scarborough, and William Alexander Waters.

Of the simpler homologues and substitution derivatives of phenazine itself, very few substances other than amino- or oxy-derivatives have been recorded in the literature, and the properties of these substances are quite unknown.

2-Methylphenazine (Merz, *Ber.*, 1886, **19**, 725; Bernthsen and Schweitzer, *Annalen*, 1886, **236**, 337), 2 : 3-dimethylphenazine (Diepholder, *Ber.*, 1909, **42**, 2922), and 2 : 6-dimethylphenazine (Bamberger and Ham, *Annalen*, 1911, **382**, 82) have been prepared, but no other homologues of phenazine are known. Of the halogen derivatives, the only substances on record are the 2 : 6-disubstituted compounds prepared from nitroso-derivatives by Bamberger and Ham (*loc. cit.*). Only two nitro-derivatives of phenazine are known, both of which may be prepared from phenazine itself (Kehrmann and Havas, *Ber.*, 1913, **46**, 347). None of these substances, however, has been obtained except in very small quantities.

With a view to the eventual examination of the properties of substituted phenazine derivatives, the known general methods for the formation of the phenazine ring system have been applied to the synthesis of certain simple substituted compounds. As a result, completed syntheses of 1-*methylphenazine* (I), 2-*methoxyphenazine* (II), 2-*chlorophenazine*, and 2-*bromophenazine* are described in the experimental portion of this paper, together with an attempted synthesis of 1-methoxyphenazine.

(I.) (II.) (III.)



Search of the literature has shown that only two *general* methods for the formation of the phenazine ring system exist: both of these have been utilised.

Of these methods, however, the condensation of an *o*-quinone with an *o*-phenylenediamine derivative (Kehrmann and Cherpillod, *Helv. Chim. Acta*, 1924, **7**, 975; Kehrmann and Mermod, *ibid.*, 1927, **10**, 62) can never be of practical value on the large scale unless the difficulties in the preparation of suitable quantities of *o*-benzoquinones can be overcome.

The alternative method of preparation of a derivative of *o*-nitrodiphenylamine, reduction to the *o*-amino-derivative, and subsequent

ring closure by eliminating 4 hydrogen atoms would appear far more suitable, but severe practical difficulties have been encountered. It has been found that the method of the final ring closure with the use of anhydrous sodium acetate, as described by Kehrmann and Havas (*loc. cit.*) for the preparation of phenazine itself, although suitable for the production of moderate quantities of this substance, is not successfully applicable for the preparation of substituted phenazines, as, in the cases studied, great charring took place and at most only traces of the desired product could be obtained. The earlier method of ring closure, by heating the *o*-aminodiphenylamine derivative with litharge (O. Fischer and Heiler, *Ber.*, 1893, **26**, 378), however, has been found of general application, except in the case of *2-amino-2'-methoxydiphenylamine*, which loses its methoxy-group, presumably by the elimination of methyl alcohol, yielding phenazine itself and not a substituted phenazine. The yields in this reaction, however, are always of the order of 5% of that demanded by the theory. As, in addition, considerable difficulty has been experienced, in the first stages of the syntheses, in obtaining satisfactory yields of certain of the *o*-nitrodiphenylamine derivatives, it cannot be said that any convenient method has yet been found for the preparation of phenazine derivatives in bulk.

The phenazine derivatives prepared are all slightly volatile in steam and sublime unchanged. They form bright yellow solutions in mineral acids, from which they may be precipitated by dilution or by neutralisation of the acid. They give no coloration with ferric chloride, in contrast to the *o*-phenylenediamines from which they have been prepared, and this difference in behaviour has been utilised as a test of the purity of the phenazine derivatives. The mono-substituted phenazines all have lower melting points than phenazine itself.

The syntheses of the methoxyphenazines are of considerable interest in connexion with the elucidation of the structure of the bacterial pigment " pyocyanine " that has been under investigation by two of the authors (J., 1923, **123**, 3278). Recent work by Wrede and Strack (*Z. physiol. Chem.*, 1924, **140**, 1; 1925, **142**, 103) has shown that pyocyanine on hydrolysis with weak alkali yields a yellow sublimable substance, " hemipyocyanine," m. p. 157°, of formula $C_{13}H_{12}ON_2$ (or possibly formula III), which yields phenazine on distillation with zinc dust. Hemipyocyanine in consequence might probably have the structure of a methoxyphenazine, or of a *C*- or *N*-methylhydroxyphenazine. Further, the yellow colour and the ease of sublimation of hemipyocyanine are both typical of the behaviour of phenazine derivatives. The synthesis

described in this paper of 2-methoxyphenazine, and the fact that it is not identical with hemipyocyanine, have eliminated one of the more probable of the formulæ for this substance.

The alternative structure of a 7-membered ring lactam (III) as suggested by Wrede and Strack (*loc. cit.*) has been considered. Attempts were made to synthesise this substance from 2-*amino-diphenylamine-2'-carboxylic acid*, but it has not yet been found possible to bring about the desired ring closure. No products have been obtained having properties resembling those of "hemipyocyanine."

Experimental.

1-*Methylphenazine* was prepared by the following methods: (*a*) 4 G. of 3-nitro-*o*-toluidine, dissolved in 200 c.c. of moist ether, were reduced to 2 : 3-tolylenediamine by means of 3 g. of aluminium amalgam, and the resulting solution was dried over fused sodium sulphate. This was then mixed with a solution of 2 g. of *o*-benzoquinone (Willstätter and Müller, *Ber.*, 1908, **41**, 2580) in 200 c.c. of dry ether and kept for 2 days over 10 g. of finely powdered fused sodium sulphate. The dark-coloured solution was shaken successively with dilute hydrochloric acid and with dilute sodium hydroxide solution till no more colouring matters were removed. The residual pale yellow ethereal layer, on evaporation, yielded a small quantity of 1-methylphenazine which, after crystallisation from hot water, melted at 108° alone or mixed with the product prepared by the alternative method (*b*).

(*b*) 2-*Nitro-2'-methyldiphenylamine* was obtained in 10% yield by heating at 220—240° for 20 hours a mixture of 50 g. of *o*-chloronitrobenzene, 70 g. of *o*-toluidine, and 50 g. of powdered anhydrous sodium acetate. The required product was separated by removing all volatile substances by steam distillation and then repeatedly crystallising the dark-coloured residue from alcohol, orange-yellow needles, m. p. 76°, being obtained (Found: C, 68·45; H, 5·3. $C_{13}H_{12}O_2N_2$ requires C, 68·4; H, 5·3%). On reduction with stannous chloride and hydrochloric acid in alcoholic solution this substance yielded the tin double salt of 2-*amino-2'-methyldiphenylamine*. This double salt was dissolved in hot alcohol, the tin hydroxide precipitated by the addition of excess of concentrated ammonia, and the free base isolated from the filtrate by dilution with water, sodium hyposulphite ($Na_2S_2O_4$) being added to prevent atmospheric oxidation of the diamine to a purple azine dye. The base crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 64° (Found: N, 14·1. $C_{13}H_{14}N_2$ requires N, 14·15%). The dry diamine, mixed with four times its weight of litharge, was heated to 200—240° under reduced pressure in a boat placed in a

long wide combustion tube. The vapours were passed through a heated column of litharge supported on pumice, to complete the reaction, and then condensed in the further cool portion of the tube. The sublimate of 1-*methylphenazine*, after further purification by distillation in steam, crystallised from hot water in pale yellow needles, m. p. 108° (Found: N, 14·45. $C_{13}H_{10}N_2$ requires N, 14·45%). The substance gave no coloration with ferric chloride. The *chloroplatinate* [Found: Pt, 23·2. $(C_{13}H_{10}N_2)_2,H_2PtCl_6,HCl$ requires Pt, 23·4%] formed fine orange needles that decomposed gradually on heating above 200°.

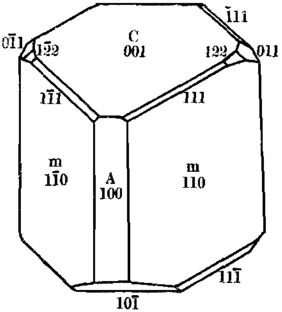
2-*Chlorophenazine* was prepared from 4′-chloro-2-nitrodiphenylamine, m. p. 146°, which was obtained from *o*-chloronitrobenzene and *p*-chloroaniline, and was then reduced to the corresponding diamine, m. p. 119° (Wilberg, *Ber.*, 1902, **35**, 957). By heating with litharge, by the method already described for the preparation of 1-methylphenazine, 2-*chlorophenazine* was obtained. After crystallisation from dilute ethyl alcohol, it formed yellow needles, m. p. 139° (Found: Cl, 16·7; C, 67·2; H, 3·4. $C_{12}H_7N_2Cl$ requires Cl, 16·5; C, 67·15; H, 3·3%). Only minute quantities of this substance could be obtained by the condensation with sodium acetate as described for phenazine by Kehrmann and Havas (*loc. cit.*).

2-*Bromophenazine* was prepared from 4′-*bromo*-2-*nitrodiphenylamine*, which was obtained in 10—20% yield by heating at 200° for 20 hours a mixture of 30 g. of *o*-chloronitrobenzene, 40 g. of *p*-bromoaniline, and 50 g. of powdered anhydrous sodium acetate, and isolated by removing all volatile matter by steam distillation, extracting the residual black solid with ether, and recrystallising the extract from a large volume of alcohol; it then formed red needles, m. p. 167° (Found: Br, 27·2. $C_{12}H_9O_2N_2Br$ requires Br, 27·3%). This substance was converted into 4′-*bromo*-2-*aminodiphenylamine* by reduction with the requisite amount of stannous chloride and hydrochloric acid in alcoholic solution. (With excess of stannous chloride, bromine was eliminated, 2-aminodiphenylamine being formed.) The pure base crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 128° (Found: Br, 30·7. $C_{12}H_{11}N_2Br$ requires Br, 30·4%). The diamine, on heating with excess of litharge, gave 2-*bromophenazine*, which crystallised from methyl alcohol in long, yellow needles, m. p. 150° (Found: Br, 30·65; C, 56·0; H, 2·7. $C_{12}H_7N_2Br$ requires Br, 30·9; C, 55·6; H, 2·7%).

2-*Methoxyphenazine* was prepared from 2-*nitro*-4′-*methoxydiphenylamine* by heating together 30 g. of each of *o*-chloronitrobenzene, *p*-anisidine, and powdered anhydrous sodium acetate at 200—220° for 16 hours (yield, 40 g.). The nitro-amine was separated by

removing all volatile matter by steam distillation, extracting the solid residue with ether, and crystallising the extract from alcohol; it formed orange-red prisms, m. p. 89° (Found: C, 63·6, 63·8; H, 5·1, 5·1. $C_{13}H_{12}O_3N_2$ requires C, 63·9; H, 5·0%). Well-formed crystals could easily be obtained from solutions in ether, and a crystallographic examination of these has been carried out by Mr. E. C. Bullard, of Clare College, in the Mineralogical Museum, Cambridge, under the direction of Professor A. Hutchinson, F.R.S., to whom the authors are indebted for the following report.

FIG. 1.



The crystals were of a typical oblique habit showing *m* (110), *C* (001) large; *x* (1̄01) medium; *A* (100), and *o* (1̄11) small; together with small faces of *r* (011); *e* (11̄1) and σ (122) on certain of the crystals.

The best faces were measured on six crystals, a one-circle goniometer being used:

Angle measured.	Mean angle.	Possible error.
A : *C* = (100) : (001)	55° 14′	12′
x : *A′* = (1̄01) : (1̄00)	74° 21′	10′
A : *m* = (100) : (110)	39° 22′	12′

From these results the calculated angular elements of the crystal are: 180° − β = 55° 14′; *a* : *b* : *c* = 1·008 : 1 : 0·799. The optical properties of the crystal were found to be: Mean refractive index = 1·73—1·74 for red light; extinction angle on plane *B* = 61° from edge *m* : *A*; optic axial angle, 2*V* = 74°; dispersion ρ<v.

On reduction of 2-nitro-4′-methoxydiphenylamine with stannous chloride and hydrochloric acid in alcoholic solution *2-amino-4′-methoxydiphenylamine* was produced, and this was isolated from the tin double salt by the method previously described for the preparation of 2-amino-2′-methyldiphenylamine. The pure base crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 78° (Found: C, 72·6; H, 6·55. $C_{13}H_{14}ON_2$ requires C, 72·9; H, 6·5%). This base, when heated with litharge according to the standard procedure already given, yielded *2-methoxyphenazine*, which crystallised from hot water in fine, yellow needles, slightly

volatile in steam; m. p. 126° (Found: C, 73·9; H, 4·7; N, 13·3. $C_{13}H_{10}ON_2$ requires C, 74·25; H, 4·8; N, 13·3%). The *chloroplatinate* [Found: Pt, 21·95, 21·9. $(C_{13}H_{10}ON_2)_2,H_2PtCl_6,2HCl$ requires Pt, 21·6%] formed fine, orange plates which gradually decomposed on heating above 250°.

Attempted Synthesis of 1-*Methoxyphenazine*.—30 G. each of o-chloronitrobenzene, o-anisidine, and powdered anhydrous sodium acetate, on heating together for 20 hours at 200°, condensed to form 2-*nitro*-2′-*methoxydiphenylamine* (20 g.), which was separated by the method used for the 4′-methoxy-isomeride. It crystallised from alcohol in red needles, m. p. 83° (Found: C, 63·8; H, 5·0; N, 11·55. $C_{13}H_{12}O_3N_2$ requires C, 63·9; H, 5·0; N, 11·5%). On reduction with stannous chloride and hydrochloric acid 2-*amino*-2′-*methoxydiphenylamine* was obtained, which crystallised from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 58° (Found: N, 13·3. $C_{13}H_{14}ON_2$ requires N, 13·1%). On heating with litharge a yellow sublimate was obtained from which only phenazine, m. p. 171°, alone or mixed with a specimen prepared by the method of Kehrmann and Havas (*loc. cit.*), could be isolated. Other methods of ring closure were attempted, none of which yielded any trace of a phenazine derivative.

Investigation of 2-Aminodiphenylamine-2′-carboxylic Acid.—2-Nitrodiphenylamine-2′-carboxylic acid (Ullmann and Maag, *Annalen*, 1907, **355**, 327; Goldberg, *Ber.*, 1906, **39**, 1691) was prepared conveniently from anthranilic acid and o-chloronitrobenzene. On reduction with stannous chloride and hydrochloric acid in alcoholic solution, the tin double salt of 2-*aminodiphenylamine*-2′-*carboxylic acid* crystallised in needles. These on decomposition with ammonia yielded a soluble salt of the acid, and the free acid was obtained on acidification. It crystallised from alcohol in plates, m. p. 204° (decomp.), and was practically insoluble in boiling benzene or boiling toluene (Found: N, 12·2. $C_{13}H_{12}O_2N_2$ requires N, 12·3%). It readily oxidised in moist air to a purple azine dye.

On passing dry hydrogen chloride into a solution in absolute alcohol, the *hydrochloride* of the amino-acid was obtained as long, colourless needles that remained unchanged even after prolonged boiling of the solution (Found: N, 10·6. $C_{13}H_{12}O_2N_2,HCl$ requires N, 10·6%) and gave ionic chlorine on treatment with water. The hydrochloride decomposed at about 240°. The same substance was obtained as the main product on treatment of the amino-acid with thionyl chloride at room temperature. There was also a small quantity of a substance easily soluble in light petroleum, from which no pure product could be isolated.

The free amino-acid, on heating at 250° for 1 hour, charred with

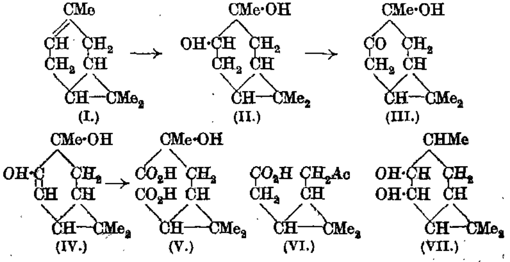
evolution of some carbon dioxide. From the residue, a green solid, m. p. 255° (decomp.), has been obtained which may possibly correspond to 4-aminoacridone (Ullmann and Maag, *Ber.*, 1907, **40**, 2522). A similar substance appears to be produced by the action of concentrated sulphuric acid on the amino-acid.

THE UNIVERSITY CHEMICAL LABORATORIES,
CAMBRIDGE. [*Received, December 10th*, 1927.]

LIII.—*The Constituents of Indian Turpentine from* Pinus longifolia, *Roxb. Part IV.*

By P. PARAMESWARAN PILLAY and JOHN LIONEL SIMONSEN.

IN Part II of this series (J., 1923, **123**, 550) attention was directed to the fact that, although the oxidation of d-Δ^4-carene with potassium permanganate in acetone solution proceeded smoothly with formation of d-1 : 1-dimethyl-2-γ-ketobutyl*cyclo*propane-3-carboxylic acid, the oxidation of d-Δ^3-carene (I) under analogous conditions did not yield the isomeric keto-acid, $C_{10}H_{16}O_3$ (VI), but proceeded in a more complex manner. The main products of the latter oxidation were two hydroxy-acids (V), the suggested mechanism of their formation being represented by the following scheme :



It appeared to us of interest to attempt (i) the preparation of the keto-acid (VI) and (ii) to determine whether the scheme outlined above actually represents the mechanism of the oxidation of the hydrocarbon.

The simplest method for the preparation of the keto-acid is the oxidation of the terpene with ozone and in preliminary experiments, made over 2 years ago, evidence of its formation was obtained. Unfortunately, owing to a breakdown in our apparatus,

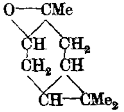
those experiments had to be temporarily abandoned and in the meantime Semmler (*Ber.*, 1927, **60**, 1591) has described the results of his experiments on the oxidation of Δ^3-carene with this reagent and has rendered unnecessary a resumption of our work.

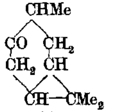
To solve the second part of our problem it was necessary to devise a convenient method for the preparation of the glycol (II). This substance is formed in small yield when *d*-Δ^3-carene is oxidised with potassium permanganate in alkaline solution (*J.*, 1920, **117**, 576), but the process is quite unsuited to its preparation in quantity. A good yield of a glycol was obtained by using hydrogen peroxide; although in the case of pinene fission of the dicyclic structure occurs (Henderson and collaborators, *J.*, 1912, **101**, 2288 *et seq.*), the main product from *d*-Δ^3-carene is carene glycol. The glycol, however, is not identical with the one previously described. When anhydrous, it has m. p. 90—91° and is optically inactive both in ethyl-alcoholic and in chloroform solution, whereas the latter has m. p. 69—70° and in chloroform solution $[\alpha]_D$ + 16·05°. The glycols may represent *cis-* and *trans*-modifications; optical isomerism, however, is not impossible, since two new asymmetric centres are formed in the oxidation. In the absence of definite evidence, we propose to call the glycol of m. p. 69—70°, *d*-carene-α-glycol and that of m. p. 90—91°, *d*-carene-β-glycol.

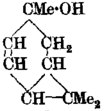
(The prefix "*d*" is retained, since the β-glycol yields optically active derivatives and the optical inactivity is therefore only "apparent.")

d-Carene-β-glycol is stable to potassium permanganate in cold acetone and is only very slowly attacked on warming. Attempts to oxidise it to the hydroxy-ketone (III) were unsuccessful. It contains, however, a secondary alcohol group, since, when heated with phthalic anhydride at 110° for some hours, it yields an *acid phthalate*. The formation of this monoacid phthalate furnishes strong evidence against the glycol having formula (VII) (compare *loc. cit.*, p. 551).

When the glycol is treated with dilute sulphuric acid it yields a mixture of *p*-cymene and an oil, b. p. 152°/100 mm., which is strongly lævorotatory. This oil appears to be l-*carene oxide* (VIII) and although it was not obtained quite pure (see p. **363**) there can be little doubt as to its constitution, since when it is heated with phthalic anhydride to 160° it yields the β-glycol acid phthalate.


(VIII.)


(IX.)


(X.)

The formation of the oxide in this way was somewhat unexpected, since it was anticipated, in view of the instability of *cyclo*hexene oxide (Brunel, *Compt. rend.*, 1903, **137**, 62), that either the isomeric ketone (IX) or the unsaturated alcohol (X) would be formed. Evidence of the formation of the ketone (IX) was, however, obtained, since the impure oxide in contact with semicarbazide acetate for some months gave a *semicarbazone*, $C_{11}H_{19}ON_3$; the quantity obtained was insufficient for the isolation of the ketone. The oxide is remarkably stable and does not undergo hydration even when shaken with sulphuric acid for some days. This stability is probably connected with the dicyclic structure containing the *gem*-dimethyl group, the marked influence of this group on ring formation having been frequently commented upon, especially by Ingold and Thorpe.

In addition to *d*-carene-β-glycol, an oil having the same composition was separated from the oxidation products of *d*-Δ^3-carene. This oil was slightly lævorotatory in chloroform solution and gave on treatment with dilute sulphuric acid, in addition to *p*-cymene, an oil consisting essentially of *l*-carene oxide. The liquid glycol was therefore probably a mixture of stereoisomerides.

l-Carene oxide is much more readily attacked by potassium permanganate in acetone solution than the glycol. The product of the reaction is a complex mixture of acids showing no tendency to crystallise. From the mixture a small quantity of a keto-acid, $C_8H_{14}O_3$, was separated in the form of its well-crystallised *semicarbazone*, m. p. 165—166°. This semicarbazone was not identical with either of the two semicarbazones of 1 : 1-dimethyl-2-β-ketopropyl-*cyclo*propane-2-carboxylic acid previously described (*loc. cit.*, p. 559), but since the semicarbazone can exist in twelve isomeric forms, this is not remarkable. The quantity of semicarbazone available was insufficient to allow of a detailed examination of the keto-acid, but the presence of the CO·CH_3 group was proved by the formation of bromoform when the keto-acid was oxidised with sodium hypobromite solution.

Some preliminary experiments have been made on the action of hypochlorous acid on *d*-Δ^3-carene: the reaction does not proceed smoothly and the products tend to decompose on attempted purification.

EXPERIMENTAL.

Oxidation of d-Δ^3-*Carene with Hydrogen Peroxide.* d-*Carene-β-glycol.*—A mixture of the hydrocarbon (1 mol.), dissolved in twice its volume of acetic acid, and hydrogen peroxide (30%; 2 mols.) was kept at 40° for some days and finally at 60° until the oxidation was complete (about 148 hours). The yellowish-brown solution

was distilled in steam to remove volatile products (acetic acid and unchanged hydrocarbon), the residue, which deposited a viscid oil on cooling, was repeatedly extracted with ether, the ethereal extracts were washed with sodium carbonate solution until free from acid (A), and the ether was evaporated. The residual oil was digested with an aqueous-alcoholic solution of potassium hydroxide * to hydrolyse any acetyl derivative present and, after addition of water, the solution was extracted with ether. From the dried ethereal extract, a viscid, brown oil was obtained which gradually crystallised in the ice-chest after addition of water. The d-*carene-β-glycol* thus obtained was washed with light petroleum (b. p. 40—60°) drained on porous porcelain to remove adhering oil (the filtrate, B, was reserved) and crystallised from much water, separating in flat prisms, frequently twinned; from light petroleum it crystallised in feathery prisms. It was readily soluble in hot water, methyl alcohol, ethyl alcohol, and benzene, and more sparingly soluble in cold water and light petroleum. The air-dried product had m. p. 75°; after drying in a vacuum over phosphoric acid, it was anhydrous and had m. p. 90—91° and b. p. 147—150°/18 mm. (Found for air-dried material: loss on drying over P_2O_5, 9·0. $C_{10}H_{18}O_2,H_2O$ requires H_2O, 9·5%. Found for anhydrous material: C, 70·4; H, 10·9. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%). The glycol was optically inactive in ethyl-alcoholic and in chloroform solutions. When treated with chromic acid in acetic acid solution, it underwent complete degradation and did not appear to yield a trace of the hydroxy-ketone; it was not attacked by hydrogen peroxide in the presence of ferrous sulphate (compare Fenton, J., 1896, **69**, 224).

The *hydrogen phthalate*, obtained by treating the glycol with phthalic anhydride at 110°, crystallised from dilute methyl alcohol in glistening prisms, m. p. 191—192° (Found: C, 67·7; H, 7·3. $C_{18}H_{22}O_5$ requires C, 67·9; H, 6·9%).

The filtrate (B) from which *d*-carene-β-glycol had been removed was distilled under diminished pressure; the main fraction passed over at 150—160°/29 mm., leaving a considerable resinous residue. On addition of a little water to the distillate and keeping in the ice-chest, a further quantity of the β-glycol crystallised. This was removed, and the filtrate redistilled; it then passed over at 155—157°/28 mm. This oil had the composition of the glycol (Found: C, 70·3; H, 10·8. Calc.: C, 70·6; H, 10·6%) and was optically active in chloroform, $\alpha_D = -0·69°$ ($c = 6·942$). When treated with dilute sulphuric acid under the conditions described below, it yielded *l*-carene oxide and *p*-cymene.

* The alkaline solution contained a small quantity of a phenol which was not examined.

The sodium carbonate solution (A) gave on acidification a mixture of acids which, after conversion into their ethyl esters, distilled irregularly from 90—180°/10 mm, and no homogeneous acid could be isolated.

l-Carene Oxide.—The glycol (60 g.) was mixed with sulphuric acid (5%; 200 c.c.) and heated on the water-bath for 48 hours; steam was passed through the solution, the volatile oil extracted with ether, the ether dried and evaporated, and the residual oil distilled under diminshed pressure (100 mm.), the following fractions being obtained; (i) 110—120° (10·5 g.), (ii) 120—140° (3 g.), (iii) 140—160° (13 g.), (iv) above 160° (5 g.).

Fraction (i) was distilled over sodium and then had b. p. 170—170·5°/685 mm., $D_{30^\circ}^{30^\circ}$ 0·8627, and $n_D^{30^\circ}$ 1·4869. These figures indicated that the hydrocarbon consisted essentially of *p*-cymene and this was confirmed by analysis (Found: C, 88·9; H, 10·7. Calc.: C, 89·6; H, 10·4%) and by oxidation to *p*-α-hydroxy*iso*propylbenzoic acid, m. p. 156—157°. Fraction (iii) on redistillation boiled at 150—160°/100 mm. and a portion, b. p. 152°/100 mm., was analysed (Found: C, 79·2; H, 10·5. $C_{10}H_{16}O$ requires C, 79·0; H, 10·5%). This fraction, which had a pleasant smell reminiscent of linalool, was evidently not quite homogeneous, as was shown by the determination of the constants of two fractions: (*a*) b. p. 150—153°/99 mm., $D_{30^\circ}^{30^\circ}$ 0·961, $n_D^{30^\circ}$ 1·4740, (*b*) b. p. 155—159°/99 mm., $D_{30^\circ}^{30^\circ}$ 0·9794, $n_D^{30^\circ}$ 1·4768, $[\alpha]_D^{30^\circ}$ − 39·16°. There can be no doubt that this substance consisted essentially of l-*carene oxide*; it did not react with the usual ketonic reagents, although, when it was kept for some months with semicarbazide acetate, a small amount of a *semicarbazone* gradually separated. It crystallised from methyl alcohol in lustrous plates, m. p. 193—193·5°, and was probably the semicarbazone of the ketone (IX) (Found: C, 63·1; H, 9·4; N, 20·4. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·1; N, 20·1%). When the oxide was heated for 6 hours at 160° with phthalic anhydride, *d*-carene-β-glycol acid phthalate was obtained in excellent yield. It had m. p. 191° and was identical in every way with the phthalate described above. The oxide was stable to bromine in chloroform solution, and to dilute sulphuric acid at the ordinary temperature.

Oxidation of l-*carene oxide*. The oxide (10 g.) was dissolved in acetone (100 c.c.) and to the solution, well cooled in ice, finely powdered and sieved potassium permanganate (27·7 g.) was added gradually, oxidation being complete in about 7 hours. The manganese dioxide sludge was collected, washed with acetone, and then repeatedly extracted with boiling water. The brown, aqueous extract was concentrated in a current of carbon dioxide, acidified,

and repeatedly extracted with ether, the viscid oil remaining on removal of the solvent was esterified in the usual manner, and the esters were distilled under diminished pressure. The main fraction, b. p. 140—160°/46 mm., was hydrolysed with methyl-alcoholic potassium hydroxide solution; the acid, isolated in the usual manner, was then obtained as a viscid oil. It was dissolved in a slight excess of ammonia and the solution was treated with calcium chloride and boiled; a small quantity of a sparingly soluble resinous salt then separated. This was removed, the solution acidified, and the acid extracted with ether. The pale yellow oil which remained on removal of the solvent yielded on treatment with semicarbazide acetate a *semicarbazone* (0·9 g.) which, after repeated crystallisation from hot water, was obtained in well-formed prisms, decomp. 165—166° (Found: C, 53·1; H, 7·9. $C_{10}H_{17}O_3N_3$ requires C, 52·9; H, 7·5%). On hydrolysis with dilute sulphuric acid, the keto-acid was obtained as a viscid oil which showed no tendency to crystallise; when it was dissolved in sodium hydroxide solution and treated with sodium hypobromite, bromoform was precipitated, but the dibasic acid formed was insufficient in quantity for examination.

Action of Hypochlorous Acid on d-Δ^3-*Carene*.—After a large number of experiments, the method briefly described below was found to be the only one to give satisfactory results.

The hydrocarbon (1 mol.) was mixed with freshly prepared sodium hypochlorite solution (2 mols.), and after the addition of an excess of boric acid the mixture was shaken mechanically until free from hypochlorous acid. The reaction product was separated by ether and purified by distillation under diminished pressure (10 mm.); two fractions were separated, (*a*) b. p. 90—93°, (*b*) 110—113°.

Fraction (*a*), which had $D_{30^\circ}^{30^\circ}$ 1·0123 and $n_D^{30^\circ}$ 1·4992, was the pure monochlorohydrin (Found: Cl, 18·5. $C_{10}H_{17}OCl$ requires Cl, 18·8%). *Hydroxychlorocarane* was a colourless oil with a fairly pungent smell. It was an extremely stable substance and was unaltered on treatment with silver oxide at the ordinary temperature. Attempts to prepare crystalline derivatives were unsuccessful.

Fraction (*b*), $D_{30^\circ}^{30^\circ}$ 1·0821, $n_D^{30^\circ}$ 1·5060, consisted of somewhat impure dichlorodihydroxymethyl*iso*propyl*cyclo*hexane (Found: Cl, 25·5. $C_{10}H_{18}O_2Cl_2$ requires Cl, 29·5%). It was a viscid oil which yielded no crystalline derivatives and was probably a mixture of isomerides derived from 1-methyl-4-*iso*propyl- and 1-methyl-3-*iso*propyl-*cyclo*hexane.

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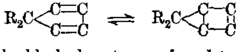
LIV.—*On the Possibility of Ring-chain Valency Tautomerism and of a Type of Mobile-hydrogen Tautomerism analogous to the Wagner–Meerwein Re-arrangement. Part I. Some Derivatives of Phorone.*

By Christopher Kelk Ingold and Charles William Shoppee.

It is now a commonly accepted view that whereas the stability and small additive power of certain ring systems containing several double linkings are to be attributed to some form of internal association of the centres of unsaturation, the numerous transformations which such systems undergo require the introduction of other phases into the general dynamic conception of their structure. Reasons for including a bridged ring in the dynamic scheme representing certain cyclic systems have recently been given. The phases (I) and (II), representing the *gem*-dialkyl*dicyclo*pentenes or *gem*-dialkyl*cyclo*pentadienes, express the dual chemistry of these substances, as, for instance, their oxidative fission to both ethylene and *cyclo*propane derivatives, and the fact that both static bridged-rings and static monocyclic compounds are formed on blocking the tautomeric system by substitution (Farmer and Ingold, J., 1920, **117**, 1362; Farmer, Ingold, and Thorpe, J., 1922, **121**, 128; Ingold, Grimwood, and Thorpe, J., 1923, **123**, 3303; Toivonen, *Ann. Acad. Sci. Fennicae*, 1927, *A*, **29**, No. 20; Ingold and Seeley, J., 1927, 1684). Further, the tautomeric substances of this series have been shown to exhibit many close analogies with aromatic compounds; and corresponding expressions representing transient forms of the aromatic nucleus have been proved possible by synthesis, and have been shown to furnish a consistent explanation of many aromatic phenomena, including the enhanced *meso*-dissociation of 9 : 10-diarylanthracenes * as compared with anthracene (Ingold, J., 1922, **121**, 1133, 1143; Ingold, Seeley, and Thorpe, J., 1923, **123**, 852; Challenor and Ingold, *ibid.*, p. 2066; Ingold and Marshall, J., 1926, 3080):

(I.)  (II.).

Excepting for the blocked systems referred to, the only bridged five-membered rings which have hitherto been studied are those

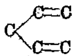
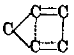
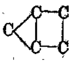
* The criticisms of Barnett, Cook, and Wiltshire (J., 1927, 1726) fail on the ground that it was not the *fact* of *meso*-dissociation but the *relative* exhibition of the phenomenon by 9 : 10-diarylanthracenes and by anthracene which was advanced as evidence of the existence of the bridged phase.

whose chemistry is complicated by their participation in an intra-annular tautomeric system. Nevertheless it is evident, in view of the situation outlined above, that considerable interest attaches to the conditions controlling the formation of static bridged-rings, and especially to instances of their preferential formation in reactions which might have been expected to yield unsaturated monocyclic or open-chain isomerides.

The reaction (I) ⟶ (II) clearly involves interaction between non-contiguous unsaturated carbon atoms. Using the term "conjugation" in a general sense to connote the yoking together of centres of unsaturation, not only when they are contiguous, but also when separated, the change implies conjugation through space and suggests the possibility of a similar conjugation between double bonds situated at a distance in open-chain olefinic compounds.* Thus a reaction such as (III) ⟶ (IV) appears possible; and, if it were reversible, it could appropriately be described as an instance of "ring-chain valency tautomerism":

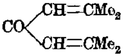
(III.) (IV.)

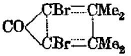
That we have been in a position to examine both reversible and complete reactions which are apparently of this type is due to the kindness of Professor F. Francis, who suggested that we should continue the investigation of phorone derivatives commenced by himself and Mr. F. G. Willson in 1913 (J., **103**, 2238). Phorone is a $\Delta^{1:4}$-pentadiene and is obviously precluded by its structure from isomerisation to a butadiene derivative; hence, any direct conjugation between the ethylenic linkings must be through space. Assuming that such a tendency exists, then, since in substituted phorones it will presumably vary from case to case, *it follows that in a sequence the extremes of which are represented* by (V) and (VII) the physical and chemical properties should vary in a manner which can be specified theoretically. Thus on passing through the series (V) ⟶ (VI) ⟶ (VII), where (VI) is a general expression representing a gradation of intermediate states, one would expect to observe diminishing colour, decreasing refractivity, decreasing parachor, diminishing unsaturation, an increasing *tendency to react in form (VII), and a decreasing tendency to* react in form (V).

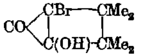
(V.)  (VI.)   (VII.)

* Certain olefinic terpenes, such as farnesene, which readily yield cyclic

Francis and *Willson* have already accumulated evidence which favours the view that certain phorone derivatives behave in the manner indicated. Phorone itself is undoubtedly mainly of type (V); *it is a bright yellow substance possessing a high refractivity* (exaltation 3 units), and a nearly normal parachor (Sugden, following paper): it is also highly unsaturated, decolorising permanganate *instantly*, adding *four atoms* of chlorine and bromine and two molecules of hydrogen bromide, yielding di*iso*butyl ketone on reduction, and giving oxalic acid, acetone, and carbon dioxide on oxidation, all in *accordance with formula* (VIII).


(VIII.)


(IX.)

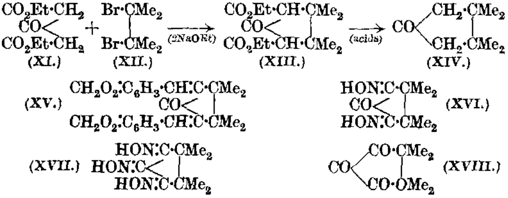

(X.)

An approach towards the saturated condition is, however, observed on passing from phorone to dibromophorone, which we regard as approximating to an intermediate condition which for the moment may be represented by formula (IX). This substance is only feebly coloured, its exaltation of refractivity is much smaller (Francis and Willson, *loc. cit.*,; see also p. 384), and its parachor abnormally low (Sugden, *loc. cit.*). Francis and Willson found it to be unattacked by mild oxidising agents, and either unaltered by reducing agents or converted in small amount into phorone; it was also unaffected by hydrogen bromide in acetic acid and by bromine in carbon disulphide. We have investigated the action of oxidising and reducing agents and find that little, if any, oxidation takes place in the presence of alkaline hydrogen peroxide, ferricyanide, or silver oxide, but that boiling alkaline permanganate causes oxidation to oxalic and acetic acids. Mild reducing agents also have no action, but vigorous reduction by Clemmensen's method yields small quantities of phorone and of deoxyphorone, a known reduction product of phorone (Claisen, *Annalen*, 1875, **180**, 6). On the other hand, Francis and Willson hydrolysed dibromophorone to a cyclic substance to which they assigned formula (X), and we have reduced it with phosphorus and hydriodic acid to a *cyclo*pentane ketone.

This ketone, which is a highly characteristic, crystalline, camphor-like substance, was previously obtained in a different way by Francis and Willson, who assigned to it formula (XIV). This is obviously in agreement with its formation from the dibromo-compound (IX); but, for reasons which will appear, it became of first importance during this investigation to make sure of the structure of the ketone and we have therefore been at pains to confirm it. Francis and Willson oxidised the substance to ααββ-tetramethylglutaric acid, and this, of course, agrees with the

suggested constitution, but does not dispose of the possible alternative structure in which the carbonyl group is next one of the CMe_2-groups. It will be shown in the sequel that the production by the reactions indicated of a ketone of the latter constitution is not inconceivable. The formation of alkylideue derivatives should decide the matter, but Francis and Willson experienced difficulty in obtaining definite condensation products with benzaldehyde and *o*- and *m*-nitrobenzaldehyde; we are, however, able to show that the ketone forms a *dipiperonylidene* derivative (XV), and a well-characterised *dioximino*-compound (XVI), which, with hydroxylamine, forms the *trioxime* (XVII) of a *substance* (XVIII) having the characteristics of a 1 : 2 : 3-triketone. These reactions, which were carried out in 1924, clearly establish formula (XIV), since the isomeric ketone could form only mono-alkylidene and mono-oximino-derivatives. Farmer and Kracovski have recently shown (J., 1927, 683) that ββ'β'-tetramethyladipic anhydride, on heating, gives Francis and Willson's ketone, which proves the same point.

A satisfactory confirmation of the structure has also been obtained by the synthesis of the ketone from tetramethylethylene dibromide (XII) and ethyl acetonedicarboxylate (XI), by way of the cyclic ketonic ester (XIII).

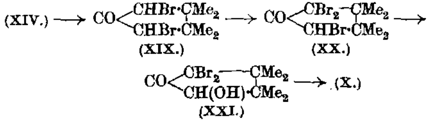


The above results may be summarised in the statement that dibromophorone (and dichlorophorone appears similar, although it was not investigated in the same detail) exhibits abnormal physical properties, *e.g.*, colour, refractivity, parachor; and, as compared with phorone, markedly diminished unsaturation. Further, it appears that, whereas on treatment with certain powerful reagents it undergoes reactions which, in so far as they indicate anything, point to a formula of the ordinary phorone type, its behaviour towards other reagents reveals a strong tendency to form closed rings. The effect of substituting phosphorus and concentrated hydriodic acid for zinc and concentrated hydrochloric acid in causing the formation of a cyclic instead of an open-chain reduction

product is noteworthy, and, along with the other physical and chemical evidence, suggests a condition intermediate between the open- and the closed-chain state.

A much more strongly marked approach towards the cyclic condition is apparent on passing to the bromohydroxy-derivative to which Francis and Willson assigned formula (X), and it is necessary now to consider the chemistry of this substance and its more immediate derivatives in some detail.

First, we have effected an independent synthesis of the bromohydroxy-compound from the ketone (XIV) by successive treatment with bromine and water. When the bromination is carried out in an anhydrous solvent, up to six atoms of bromine are absorbed and hydrogen bromide is evolved. During the process a crystalline bromide is produced and may separate, but our efforts to isolate *and analyse it failed owing to the rapidity with which it decomposed* into an oil containing between two and three atoms of combined bromine. We are not at present prepared to express any view as to the constitution of this intermediate product, beyond that it consists at least in part of a substance which, on treatment with water, gives the bromohydroxy-compound (X). When the bromination is incomplete (we suspect that it is affected by the fortuitous crystallisation of the solid bromide), as indicated by the smaller bromine-content of the residual oil, the change effected by water is also incomplete, and an unreactive compound containing two atoms of combined bromine remains. On further bromination this is converted into the precursor of the bromohydroxy-compound. Though modifications are possible, the following scheme is regarded as approximating to the observations, the compound (XIX) representing the unreactive, and (XX) the reactive, bromination product:

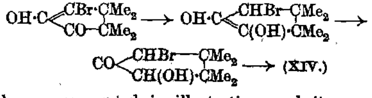


The elimination of hydrogen bromide from (XXI) is in accordance with analogy. Evidence of interaction between the α- and α′-positions of a cyclic ketone was encountered by Wallach (*Annalen*, 1917, **414**, 296) in the case of *cyclo*hexanone derivatives, and in the present instance the tendency to a reaction of this type would be expected to be increased by the accumulation of *gem*-dimethyl groups. The fact that, even where excess of bromine is employed,

only six and not eight atoms are involved is also in accordance with Wallach's observations on the halogenation of cyclic ketones (*Annalen*, 1905, **343**, 41), and may be compared with the difficulty often experienced in replacing this last available hydrogen atom in a keto-enol system (compare Dieckmann, *Ber.*, 1894, **27**, 954; 1897, **30**, 1471; Thorpe, numerous papers); it is also possible that higher bromination products are formed, but immediately bridge with the elimination of elemental bromine, as is suggested by the experiences of Guareschi (*Atti R. Accad. Sci. Torino*, 1910—1911, **46**, 662) and Meerwein (*J. pr. Chem.*, 1922, **104**, 161), thus giving a smaller net absorption. However this may be, it is evident that the process involves no re-arrangement of the carbon skeleton, since the bromohydroxy-compound on reduction both by acid and by alkaline reagents yields the original tetramethyl*cyclo*pentanone (XIV).

We have taken the view that this complete synthesis, even when taken together with Francis and Willson's degradation of the bromohydroxy-compound to tetramethylsuccinic acid, does not fully establish their formula for the compound; for although that formula certainly provides the simplest interpretation of the facts, the latter concern a field of organic chemistry in which subtle changes are possible, so that caution is necessary in drawing conclusions as to structure. We do, however, regard the following features as having been definitely diagnosed: (i) the presence of the *cyclo*pentane ring, (ii) the adjacent situation of the two *gem*-dimethyl groups, (iii) the unsymmetrical situation of the bromine atom with respect to the *gem*-groups, (iv) the symmetrical situation of one oxygen atom with respect to the *gem*-groups, (v) the presence of a hydroxyl group. In addition to formula (X), there is another formula which embraces all these conclusions, namely (XXII), and this can be brought into harmony with the reduction to the symmetrical *cyclo*pentane ketone (XIV), because preliminary 1:4-addition of hydrogen, followed by ketonisation and further reduction, could bring about the necessary alteration in the position of the carbonyl group:

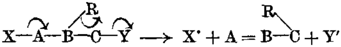
(XXII.)



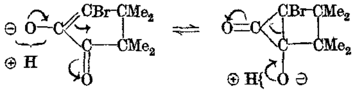
The scheme represented is illustrative, and its essentials are independent of any particular supposition regarding the stage at which the halogen is removed from the molecule. Further, formula (XXII) is not inconsistent with the evidence of synthesis; for the

two formulæ (X) and (XXII) are more closely related than appears at first sight, in that, although they are distinct in framework and differ in the position of a hydrogen atom, the latter is ionisable in either case, and hence potentially mobile, and the two carbon skeletons are related like those of the factor and product of a Wagner re-arrangement.

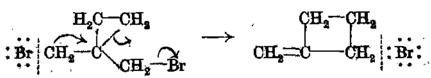
Considerations based on the electronic theory of valency lead us to formulate the pinacol–pinacolin, Wagner–Meerwein, and related transformations, such as the *pinacolic deamination*,* by the following general scheme :—



in which the tendency of X to part from, and Y to hold, electrons during ionisation or combination with a reagent supplies the driving force of the reaction. In the case under discussion, if we assume preliminary ionisation, the electron repulsion of the negative pole collaborating with the electron attraction of the neighbouring carbonyl group might provide the impetus necessary for the interconversion of the structures :

(XXIII.)  (XXIV.)

The postulated change in either direction may be compared with the formation of methylene*cyclo*butane (B) from ωω′-dibromo-1 : 1-dimethyl*cyclo*propane (A) and zinc (Ingold, J., 1923, **123**, 1756) on the supposition that an atom of metallic zinc first removes an atom of bromine with a *sextet* :

(A)  (B)

* Here the electron sink, Y, is presumably the positive pole of the diazonium ion formed by the action of nitrous acid (compare Baker, Cooper, and Ingold, this vol., p. 426). Similarly in the benzil–benzilic acid change the electron sink, X, is the negative pole formed by the addition of hydroxide ion :

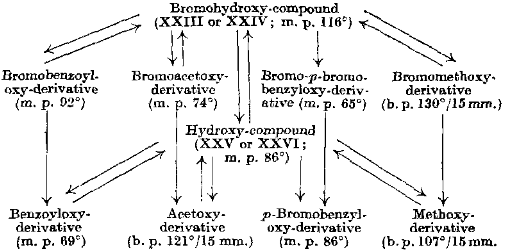
Thus, tautomerism between the structures (XXIII) and (XXIV) is readily conceivable, and the problem of distinguishing between them becomes in the first instance that of ascertaining the position or positions occupied by each of the characteristic groups by the study of suitable derivatives.

Francis and Willson found that when the bromohydroxy-compound was reduced with zinc dust and glacial acetic acid the bromine atom was replaced by hydrogen and a compound was formed which closely resembled the halogenated parent and evidently possessed a similar constitution. All our experiments confirm that conclusion; we have, for instance, regenerated the original bromohydroxy-compound by directly brominating the bydroxy-compound. Further, the derivatives formed by the bromohydroxy-compound resemble the corresponding derivatives of the hydroxy-compound; for instance, the latter, on acetylation, gave the same compound as that which Francis and Willson obtained by reduction of the acetyl derivative of the bromohydroxy-compound. Similarly, the bromobenzoyloxy-compound, the *bromomethoxy*-compound, and the *bromo*-p-*bromobenzyloxy*-compound, which were prepared directly from the bromohydroxy-compound, on reduction gave *benzoyloxy*-, *methoxy*-, and p-*bromobenzyloxy*-derivatives which were also obtained from the hydroxy-compound by acylation or alkylation. It is evident, then, that the constitutions of the halogen compounds are referable to those of the corresponding hydrogen derivatives (with the reservation mentioned on p. 379), and we have therefore concerned ourselves mainly with the bromine-free hydroxy-compound (XXV or XXVI) in the investigation, described below, regarding the respective functions of the two oxygen atoms contained in the complex:

(XXV.) $OH\cdot C{<}\begin{matrix}CH\cdot CMe_2\\ CO\cdot CMe_2\end{matrix}$ $\qquad$ $CO{<}\begin{matrix}CH{-\!\!-}CMe_2\\ C(OH)\cdot CMe_2\end{matrix}$ (XXVI.)

First, it should be stated that the alkyl and acyl compounds mentioned above are actually *O*-derivatives, and not *C*-derivatives, because the alkyl and acyl groups can readily be removed. For example, the bromoacetoxy- and bromobenzoyloxy-compounds are hydrolysed by acids, and the corresponding hydrogen derivatives by alkaline hydrolysing agents. The methyl group in the bromomethoxy-compound can be eliminated by the Zeisel method. The corresponding experiment was not tried with the bromo-*p*-bromobenzyl derivative, the same point having been proved for this compound at an early stage in the investigation through the observation that on ozonolysis the alkyl group appears in the form of *p*-bromo-

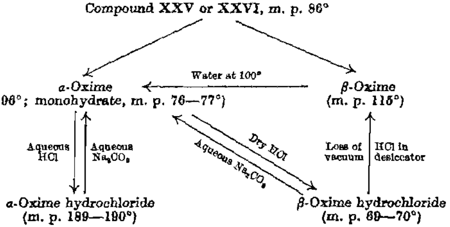
benzaldehyde. These relations are summarised in the following scheme :



In contrast with the close similarity between the bromohydroxy-compound and the bromine-free hydroxy-derivative in their hydroxylic reactions, these two substances differ notably in the degree to which they exhibit ketonic properties. In fact, neither Francis and Willson nor we have been able to obtain an oxime or semicarbazone of the bromohydroxy-derivative, and we have similarly failed in the case of all its derivatives in which a bromine atom is attached to the five-membered ring; yet on any probable view of the constitution of these substances a ring-bound carbonyl group must be present. On the other hand, the compounds of the reduced series all form oximes with moderate ease; indeed, from the parent hydroxy-derivative we obtained two *oximes* as well as a *semicarbazone*. In our view this remarkable difference is to be attributed, not to some fundamental difference of constitution, but to the inhibiting effect of the bromine atom. Oximation is a reaction notoriously sensitive to constitutional influences, and the strong inhibition (probably polar as well as steric) produced by bromine and chlorine in halogenated ketones is often such as to prevent oxime formation altogether. On the other hand, we are unwilling to employ the facts referred to as the basis of any constitutional argument regarding the relative positions of the bromine atom and carbonyl group in the bromo-compound (XXIV or XXIII), since the possibility of "short-cuts" for the transmission of polar influences in compact ring-structures cannot be disregarded.

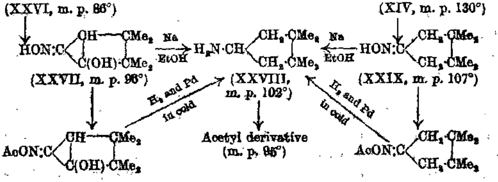
Our attention was first focussed on the two oximes in view of the possibility that they might be position-isomerides representing the two forms (XXV and XXVI) of the parent. This, however, was not the case, since the two oximes were found to be interconvertible

directly (β ⟶ α) and through the hydrochloride of one of them (α ⟶ β) in accordance with the following table :



Hence it appeared that the two compounds are *stereoisomeric*, and that the oximino-group is attached to the same nuclear carbon atom in each ; it remained to determine which one.

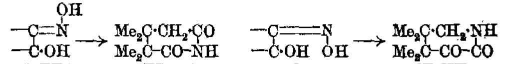
This was done by completely reducing the α-oxime (m. p. 96°) to a tetramethyl*cyclo*pentylamine. We found that sodium amalgam in boiling glacial acetic acid, and sodium in hot alcohol, effected the change smoothly, and that the same result could be obtained equally satisfactorily without the use of high temperatures by reducing the *acetyl* derivative of the oxime with gaseous hydrogen in the presence of colloidal palladium. The free *base* (XXVIII), a volatile crystalline solid, together with its *hydrochloride*, *picrate*, *chloroaurate*, and *acetyl* derivative, were identical, each to each, with the corresponding compounds prepared by applying the same three methods of reduction to the *oxime* (XXIX) (or its *acetate*) of the symmetrical ketone (XIV). Therefore, formula (XXVI) being adopted as a basis of representation, the reactions may be expressed as follows :



The orientation of the oximino-group in (XXVII), and of the amino-group in (XXVIII), thus depend on the constitution ascribed to the ketone (XIV), which was established in two independent way

and is therefore beyond doubt. Although the experimental evidence is thus complete, the whole of it is further strengthened by the fact that, by methods described below, we have been able to prepare the isomeric unsymmetrical *ketone*, having its carbonyl group adjacent to one of the CMe_2-groups, its *oxime*, the corresponding unsymmetrical *amine* and its salts and *acetyl* derivative, all of which are easily identified crystalline compounds, as are the isomerides of the symmetrical series. We conclude that in the hydroxy-compound, m. p. 86°, the group exhibiting ketonic reactivity is that situated symmetrically with respect to the two *gem*-dimethyl groups in the carbon skeleton.

With regard to the space configurations of the two oximes (XXVII) we are able to advance the following evidence. On Meisenheimer's theory of *trans*-interchange, the two oximes might yield the following internal amides under the conditions of the Beckmann transformation :

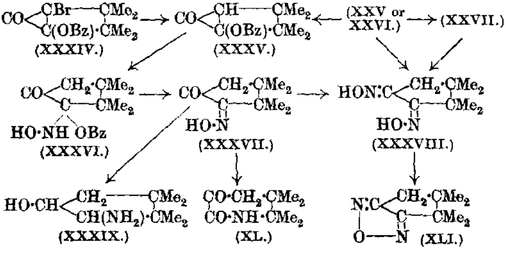


(XXX.) (XXXI.) (XXXII.) (XXXIII.)

Under the conditions in which we have effected a change of this type the α-oxime passes into its β-isomeride, and is therefore not available for the experiment. On the other hand, the β-isomeride, on treatment with excess of dry hydrogen chloride in a warm solvent, yields a re-arrangement *product* which apparently possesses formula (XXXIII). Its properties are in agreement with this constitution, and it is not the *imide* (XXXI), for we have prepared the latter by the action of gaseous ammonia on *ααββ-tetramethylglutaric anhydride*. If this interpretation is correct, it follows that the α-oxime, m. p. 96°, is to be regarded as having the configuration (XXX), and the β-oxime, m. p. 115°, is represented by (XXXII). It should be remarked that the β-oxime (but not the α-) gives a strongly coloured iron salt, in which the iron is conceivably chelated (compare formula XXXII).

Turning to the acyl derivatives of the bromohydroxy-compound and its halogen-free analogue, the benzoyl derivatives offered an attractive point of attack, since both are crystalline and possess all the characteristics of pure compounds. Both substances appear to be saturated. Thus neither responds to the Baeyer test for unsaturation, and neither absorbs bromine in chloroform. It is true that the bromobenzoyloxy-compound is attacked by zinc dust and acetic acid, but the reduction stops abruptly after the bromine atom has been replaced by hydrogen, the nucleus being unaffected.

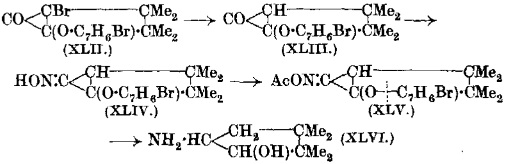
When the halogen-free benzoyl compound is treated with hydroxylamine, one molecule of this reagent is taken up and one of benzoic acid is simultaneously eliminated. This takes place in the cold under conditions which preclude ordinary hydrolysis of the acyl group, and we therefore infer that it is the hydroxylamine which has displaced the benzoyl radical. The compound formed (m. p. 115°) is isomeric with, and different from, the α- and β-oximes of the symmetrical series (mixed m. p. depressions), which were prepared from the parent hydroxy-compound without previous benzoylation, and is evidently the unsymmetrically oximinated analogue, since (*a*) it yields the original hydroxy-compound (m. p. 86°) on hydrolysis, and (*b*) on prolonged treatment with hydroxylamine it gives the same dioximino-compound as that prepared by further oximination of the symmetrical α-oxime. It is consistent with this interpretation that the new *monoxime* (XXXVII), on re-arrangement, gives an internal *amide* (XL) isomeric with the amide and imide mentioned above (XXXI and XXXIII) and that the *dioxime* (XXXVIII) readily yields a *furazan* (XLI). On reduction with sodium and boiling alcohol the new monoxime gives the *hydroxy-amine* (XXXIX). The whole series of observations corresponds with Francis and Willson's formulation of the bromo-hydroxy- and hydroxy-compounds, and may accordingly be represented as follows:



It must be pointed out that the above scheme for the orientatio of the benzoyloxy-group in (XXXIV) and (XXXV) is dependent o the correctness of the inference that, because hydroxylamir displaces the benzoyl radical, the oximino-group therefore occupi that nuclear position from which the extruded group has be removed. Such a substitution of groups might take place throu ... addition of hydroxylamine giving the addition produ

(XXXVI), the subsequent irreversible decomposition of which is determined by the stability of the benzoate ion. We are not prepared to go further than to say that these assumptions seem to us plausible, and that we regard the orientation as tentative only.

The *p*-bromobenzyloxy-derivatives both of the bromohydroxy- and hydroxy-series are also crystalline, behaving in all respects as pure compounds, and closely resembling the benzoyl derivatives in their indications of saturated character. The bromo-*p*-bromobenzyloxy-compound (XLII) on reduction by zinc and acetic acid is converted into the *p*-bromobenzyloxy-derivative (XLIII), which is formed without by-products and appears to be incapable of further reduction by this method. It forms an *oxime* (XLIV), and, as might be expected, there is little or no tendency towards extrusion of the *alkyl* group. We have not yet succeeded in establishing satisfactory conditions for the reduction of the oxime itself, but its *acetyl* derivative (XLV), on reduction with sodium and boiling alcohol, yields a saturated *hydroxy-amine* (XLVI), isomeric with (XXXIX). These reactions may be formulated as follows, the interpretation being dependent on that applied to the benzoyl compounds :

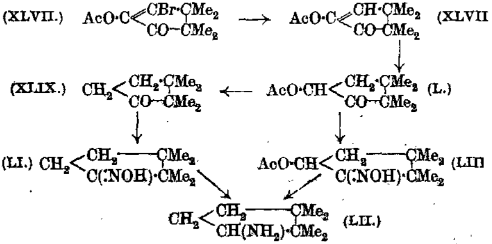


It is now necessary to consider some derivatives of the bromohydroxy- and hydroxy-compounds which exhibit some remarkable differences of behaviour as compared with the acyl and alkyl derivatives just mentioned. The group of compounds referred to includes the acetoxy-derivatives, the methoxy-derivatives, and probably also the liquid by-product which was obtained (see p. 388) along with the crystalline main product on alkylation of the bromohydroxy-compound with *p*-bromobenzyl bromide.

These compounds are conspicuously unsaturated. They are all oils, excepting the bromoacetoxy-derivative, which is crystalline; and for this reason we have examined the acetoxy-compounds in greater detail than the others. In illustration of the unsaturated character of these substances, the bromoacetoxy-compound rapidly reduces cold alkaline permanganate under conditions in which the bromobenzoyloxy-compound causes no perceptible reduction over

an extended period. The acetoxy-compound rapidly absorb bromine in cold chloroform, in contrast with the benzoyloxy compound, which remains unaffected under these conditions, and even on boiling, is extremely slowly attacked. Again the acetoxy compound is reduced by zinc dust and acetic acid to a *dihydro* derivative, whereas the benzoyloxy-compound, as already men tioned, is unaffected by this treatment.

These contrasts suggest that the bromoacetoxy- and acetoxy compounds may be derived from the unsaturated, monocyclic form of their respective parents; and in support of this view we are abl to advance the following experiments, which appear to orient th acetoxy-group in the symmetrical position with respect to the pai of *gem*-dimethyl groups. The bromoacetoxy-compound was reduce in the following stages with successive treatments with zinc c sodium amalgam in glacial acetic acid: bromoacetoxy-compoun $\xrightarrow[(2H)]{}$ HBr + acetoxy-compound $\xrightarrow[(2H)]{}$ dihydroacetoxy-compoun $\xrightarrow[(2H)]{}$ H·OAc + dihydro-compound. The final product, which a saturated ketone, $C_9H_{16}O$, proved to be, not the symmetric tetramethyl*cyclo*pentanone already described, but its unsymmetric *isomeride* (XLIX) (*vide infra*). It was converted into its *oxime* (LI which was reduced with sodium and alcohol to the unsymmetric *tetramethyl*cyclo*pentylamine* (LII). Finally the *oxime* (LIII) of tl dihydroacetoxy-compound (L) was completely reduced, and tl product identified as the same tetramethyl*cyclo*pentylamine. If tl monocyclic unsaturated formulæ (XLVII) and (XLVIII) be adopt for the bromoacetoxy- and acetoxy-compounds respectively, tl above relationships are capable of explanation on the followi lines:



The symmetrical and unsymmetrical ketones (XIV and XLI are superficially extremely similar (both have the appearan odour, and large volatility of camphor), but are readily distinguisl

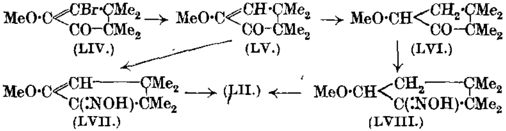
because they depress one another's m. p.'s, as do the derived oximes and semicarbazones. Both ketones, on oxidation with dilute nitric acid, yield ααββ-tetramethylglutaric acid, and this, taken in conjunction with the work already described on the symmetrical ketone, establishes the constitution of the unsymmetrical ketone. The two tetramethyl*cyclo*pentylamines are also crystalline, although on account of their volatility, we have, to conserve material, usually handled them in the form of their picrates or acetyl derivatives, which also give mixed m. p. depressions. The following comparison of m. p.'s illustrates the general similarity of the isomerides :

	Ketone.	Oxime.	Oxime hydrochloride.	Semicarbazone.	Amine.	Picrate.	Chloroaurate.	Acetyl derivative.
Symmetrical ...	130°	107°	119°	224°	100—102°	225°	230°	95°
Unsymmetrical	119	102	125	222	Not taken.	243	197 *ca.*	115

Although the ketone (XLIX) is undoubtedly the main product of the reduction represented in the scheme formulated above, it is usually accompanied by a small, but detectable, quantity of the isomeric symmetrical ketone (XIV) (for separation, see p. 397). In this connexion it may be remarked that, theoretically (and also practically), an essential condition for the preparation of the unsymmetrical ketone by the method outlined is that the acetyl group should remain attached to the molecule during the first two stages of the reduction; this follows from the tautomeric hypothesis relating to the cyclic hydroxy-ketones, for the formation by hydrolysis of a free hydroxyl group would liberate the mobile system, the reduction product of which is known to be the symmetrical ketone (XIV). It was for this reason that glacial acetic acid was employed as medium throughout the reductions, and that the intermediates (XLVIII) and (L) were purified and analysed in order to confirm the integrity of their ester groups. On the other hand, although the bromoacetoxy-compound appears to be a single individual, its reduction products (XLVIII) and (L) are liquids, and, despite their constant boiling points, it cannot be asserted that they do not contain isomerides. The migration of acyl groups is such a common experience that the possibility must be considered, but whether the appearance of the symmetrical ketone as a by-product is actually to be ascribed to tautomeric mobility of the acetyl groups under certain conditions, or to some undiscovered mechanism, cannot, we think, be decided on the evidence. We are likewise open-minded with regard to the possibility of the migration of *O*-alkyl groups during the reduction of the bromo-alkyloxy-compounds.

The bromomethoxy-compound (LIV) is unstable to permanganate

and, like the bromoacetoxy-derivative, can be reduced by zinc and acetic acid, not only to the halogen-free parent (LV), but also to the *dihydro*-derivative of the latter (LVI). The methoxy-group in the dihydro-compound cannot be eliminated by continued treatment, but since both the *oxime* (LVII) of the methoxy-compound and *that* (LVIII) of the dihydromethoxy-compound yield the unsymmetrical tetramethyl*cyclo*pentylamine (LII) on reduction with sodium in alcohol, we infer that the methyl and acetyl derivatives of the bromohydroxy- and hydroxy-compounds possess corresponding structures:



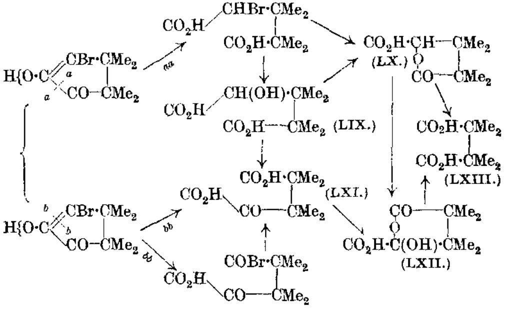
Summarising the above experiments on the substitution products of the bromohydroxy-compound, it appears that Francis and Willson's conception of that substance requires extension by the introduction of the alternative unsaturated formula (XXII).

Further evidence tending in this direction has been obtained by continuing the study, commenced by Francis and Willson, of the behaviour of the parent bromohydroxy-compound itself in the presence of reagents towards which it would be expected to reveal any unsaturated character it possessed.

The first series of experiments along these lines relates to oxidation. Francis and Willson used alkaline permanganate and obtained the lactonic acid (LXII) (compare Rothstein and Shoppee,* J., 1927, 531), formed by additive ring closure of the ketonic acid (LXI). We have obtained the same lactonic acid by employing also alkaline chlorate in the presence of osmium tetroxide, alkaline ferricyanide, and alkaline hydrogen peroxide. Using alkaline chlorate and osmium tetroxide, we have isolated, in addition, the lactonic acid (LX) of the dibasic hydroxy-acid (LIX). Oxidation with chromic anhydride or chromic acid (Francis and Willson) causes complete degradation to tetramethylsuccinic acid (LXIII).

* The opportunity may be taken to mention that in the light of observations recorded on p. 406, Rothstein and Shoppee now regard the compound, previously considered to be methyl γ-keto-ααββ-tetramethylglutarate, as the lactone of methyl hydrogen γ-hydroxy-γ-methoxy-ααββ-tetramethylglutarate, $\overline{CO\cdot CMe_2\cdot CMe_2\cdot C}(OMe)\cdot CO_2Me$ (O bridging CO and C), *a conclusion which further strengthens their case in favour of the cyclic constitution of the homologues of Balbiano's acid and its derivatives.*

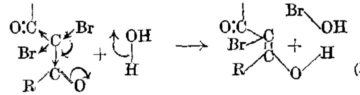
The interpretation of these results in terms of the unsaturated formula of the bromohydroxy-compound is not compulsory; nevertheless, we believe that this structure affords the more satisfactory basis for explanation, having regard to the sensitivity towards oxidising agents of the methyl and acetyl derivatives. Also, in view of the fact that the attack of mild oxidising agents usually proceeds much more smoothly in alkaline than in neutral solution, we suspect that degradation occurs most readily through the ion. These and other considerations relating to the observations lead us to advance the following general scheme for the oxidation of the bromohydroxy-compound :



It will be understood that this scheme is based partly on direct evidence and partly on indirect evidence or analogy. As an illustration of the use which has been made of the latter, the following point may be considered. When ozonised oxygen is passed into a chloroform solution of the bromomethoxy-compound, elementary bromine is eliminated, proving that the :CBr-group is involved in the attack; the product obtained on decomposing the ozonide is the hydroxy-lactonic acid (LXII). On the other hand, when the bromoacetoxy-compound is treated with ozone under similar conditions, the bromine atom remains attached to the molecule until the ozonide is reduced with zinc dust. Now the attack at the :CBr-group with fission at *bb* is probably dependent on the process X—C=CBr, the effectiveness of which should vary according to the value of X as an electron-source. The theoretical order, $O^{\ominus} > OMe > OAc$, being known, the inference, as regards the ion, is obvious.

We have further examined the behaviour of the bromohydroxy-compound towards halogens. Francis and Willson observed that on bromination in acetic acid a dibromo-compound is formed to which they ascribed formula (LXVI); since, however, one bromine atom (and only one) is readily removed by hydrolysis in the form of *hypobromous acid, the original bromohydroxy-compounds being regenerated, they also recognised a possible tautomeric form* represented by the alkyl hypobromite structure (LXIX); and having regard to our evidence in favour of the monocyclic formula of the bromohydroxy-compound, it is necessary to envisage the possibility (LXX) in addition.

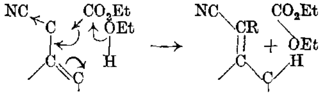
Lauer has recently shown that tribromophenol bromide and its congeners, which exhibit the same peculiarity in regard to hydrolysis, are actually aryl hypohalites (*J. Amer. Chem. Soc.*, 1926, **48**, 442), and not halogeno-quinone derivatives, as had previously been supposed (Thiele and Eichwede, *Ber.*, 1900, **33**, 673). On the other hand, Norris and Thorpe have proved (J., 1921, **119**, 1199) that the dihalogeno-derivatives of dihydroresorcinol homologues, which also exhibit the peculiarity, are not hypohalites but 2 : 2-dihalogeno-1 : 3-diketones. It follows that the exhaustive halogenation of ketones can give rise to both types of structure, and that the elimination of one atom of halogen as hypohalous acid on hydrolysis is not (contrast Vorländer, *Annalen*, 1897, **294**, 253), a criterion which will decide between them. The abnormal hydrolysis *of the dihalogeno-diketones may be regarded as a six-cycle promoted* by the electron affinity of the groups attached to the halogen-bearing carbon atom :

(LXIV.)  (LXV.)

Obviously the process cannot be repeated with the second bromine atom originally present in (LXIV), for it cannot occur with the enol (LXV), and, if this were ketonised, a repetition would merely enolise it again, since the forces operate to remove the atom (hydrogen) which most readily parts with electrons. This accounts for the dissimilar behaviour of the two bromine atoms, and expresses *Norris and Thorpe's suggestion that the elimination of the halogen* is fundamentally concerned with the tendency of the system to acquire a mobile hydrogen atom.* It also follows that, if two

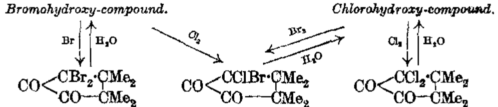
* [Added in proof] Soper and Smith's interesting experiments (this vol., p. 139) suggest that the hydrolysis of aromatic chloroamines may be analogous.

different halogen atoms are attached to the central carbon atom, the product of hydrolysis will retain that which has the greater affinity for electrons (F>Cl>Br>I). Obviously the water molecule might act as such or as H˙ and OH′ ions. A similar explanation may be given of the elimination of carbethoxyl as ethyl carbonate from cyano-esters (Rogerson and Thorpe, J., 1905, **87**, 1702; Ingold and Thorpe, J., 1919, **115**, 143)

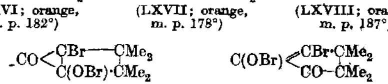


and this shows why the βγ-double bond is necessary, why the group R is necessary (since otherwise hydrogen would be removed), and why a βγ-unsaturated cyano-ester yields an αβ-unsaturated nitrile (Kon and Narayanan, J., 1927, 1536).

We find that Francis and Willson's dibromo-compound is actually the dibromo-diketone (LXVI), and is not an alkyl hypobromite (LXIX or LXX). For the derivative obtained by chlorinating the bromohydroxy-compound is identical with that prepared by brominating the chlorohydroxy-compound, which shows that the halogen atoms in the common *product* (LXVII) are in structurally equivalent positions; further, this derivative, the *dichloro*-compound (LXVIII), and the dibromo-compound, are so *very* closely similar (see table) that the same conclusion must, we think, be applied to the latter two. As would be expected, the chlorobromo-diketone, on hydrolysis, yields the chlorohydroxy-compound exclusively:

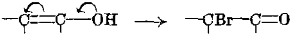


(LXVI; orange, m. p. 182°) (LXVII; orange, m. p. 178°) (LXVIII; orange, m. p. 187°)

(LXIX.)  (LXX.)

Here, as with oxidation, one is not compelled to interpret the reactions on the basis of the monocyclic unsaturated formula for the bromohydroxy-compound, but, nevertheless, there are good grounds for doing so. According to Orton, Hughes, and Watson (J., 1927, 2461), the bromination of a ketone takes place by direct

β-bromine-substitution of the enol, the product being necessarily ketonic :



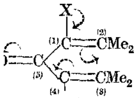
The reaction is assumed to occur on " activation " of the enol, and one form which activation might conceivably assume would be the ionisation of the hydroxyl group with the production of a strongly electron-repelling negative pole. This may be the significance of the observation that, whereas the dihalogeno-diketones are readily produced by halogenation in cold acetic acid (ionising solvent), they cannot be prepared in pure chloroform or carbon disulphide (non-ionising solvents) (compare Francis and Willson). Taking the view that in the bromination, as in the oxidation, of the bromohydroxy-compound, the reactive individual is probably the ion, and, accepting Orton, Watson, and Hughes's mechanism, the constitutions (LXVI—LXVIII) follow automatically.

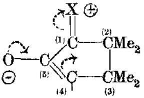
It is now possible to develop the suggestion made on p. 368 that dibromophorone represents a balanced example of ring-chain valency tautomerism. In its chemical properties it has much in common both with phorone and with its fully cyclised oxygenated derivatives. Sugden's parachor determinations provide interesting physical evidence pointing to an intermediate condition, and some additional confirmation from the physical side is provided by refractivity data :

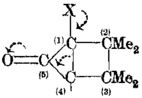
	Exaltation (λ 5893) for		
Phorone	3·04	4·77	5·32
Dibromo-derivative	1·37	3·10	3·65
Dichloro-derivative	0·30	2·03	2·57
Acetoxy-derivative	−1·52	0·21	0·76

The varying action of different substituents in favouring to different degrees the cyclic form of the phorone system arises, we believe, from their different electron-giving tendencies. An electron-giving group in position (1) (LXXI), collaborating with the elctron-attracting carbonyl group in position (5), will produce a series of mutually dependent displacements of the labile electrons of the double bonds (1—2) and (3—4), giving as the first stage of space-conjugation a partial valency between the carbon atoms (2) and (3) (LXXI). If the tendency to this change is sufficient, the molecule may reach or approximate to the dipolar condition, represented by (LXXII), in which the labile double-bond-electrons are now at (4—5), and are subject to simultaneous repulsion by the negative charge at (5) and attraction towards the positive charge at (1). This condition corresponds to a partial valency between (4) and (1),

ınd depolarisation in the direction of the potential gradient might stablish the bond (4—1) (LXXIII). Formula (LXXII), then, nay be taken to represent a whole range of states on either side of he dipolar condition; its equilibrium with (LXXI) exemplifies the onception of ring-chain valency tautomerism, and its equilibrium vith (LXXIII) that of tautomerism correspouding with the Wagner e-arrangement. It is evident, also, that any mechanism for xternal depolarisation (*e.g.*, association with another ion) might ıbviate the necessity for internal re-adjustment.


(LXXI.)


(LXXII.)


(LXXIII.)

According to this view, the tendency of a substituted phorone to lose up should run parallel with the basicity (tendency to become hared) of the unshared electrons in X; and, for the groups, X, xamined, the order of the effect, as indicated, for instance, by *p*-directive power in aromatic substitution, should be OR> alogens>H, which agrees with the observations.

EXPERIMENTAL.

[*Note*: The analysis of many of the compounds described in this ection gave difficulty until it was discovered that by the use of uprous chloride (Haas, J., 1906, **89**, 570) the escape of unburnt ıethane and ethane could be avoided and correct results obtained. [ost of the carbon and hydrogen estimations recorded below were ırried out by Haas's method.]

αα-Dibromophorone (1 : 4-*Dibromo*-2 : 2 : 3 : 3-*tetramethyl*-[0,1,2]-icyclo*pentanone*).—This was prepared in the manner recommended y Francis and Willson (yields 80—88%; m. p. 32°). It is ecessary that the phorone tetrabromide (yields 80—90%; m. p. 3°) should be perfectly pure and our practice was to crystallise it ıree times from alcohol before conversion.

Care being taken to avoid accidental inoculation, dibromo-horone, when fused and cooled to 20°, remains liquid long enough ı enable its density and refractive index to be determined. We ıund $d_4^{20°}$ 1·5727, and $n_D^{20°}$ 1·54766, whence $[R_L]_D = 59·74$. Francis ıd Willson, working at 37°, obtained $[R_L]_D = 59·77$. The exalt-ions recorded on p. 384 are calculated from Eisenlohr's (1910) omic and structural constants and our observed value for $[R_L]_D$.

Reduction of Dibromophorone to Phorone and Deoxyphorone.

Dibromophorone was reduced with amalgamated zinc and boiling concentrated hydrochloric acid (compare Clemmensen, *Ber.*, 1913, **46**, 1837). In the early stages of the process phorone distilled from the short condenser employed. After 2 hours the product was distilled in steam, the distillate extracted with ether, and the deoxyphorone thus obtained purified by washing with a little ligroin and crystallisation from alcohol; m. p. 190° (Found: C, 82·9; H, 10·7. Calc.: C, 83·0; H, 10·8%). The portion of the reduction product which did not distil in steam was a yellow, viscous oil, which decomposed on attempted distillation at 2 mm. It decolorised permanganate, but did not yield a semicarbazone or other crystalline derivative.

Reduction of Dibromophorone to 3 : 3 : 4 : 4-*Tetramethyl*cyclo*pentanone.*—Dibromophorone (25 g.), hydriodic acid (250 g.; *d* 1·7), and red phosphorus (30 g.) were boiled together under reflux for 4 hours and the product was distilled in steam. Owing to the volatility of tetramethyl*cyclo*pentanone in ether vapour, it was found advantageous to proceed with its isolation without the use of ether. The first 50 c.c. of distillate, which contained the bulk of the ketone, were therefore collected separately and saturated with ammonium sulphate; the oil was then removed, dried directly with calcium chloride, and distilled; b. p. 190—195°; m. p. 130° (Found: C, 76·7; H, 11·5. Calc.: C, 77·1; H, 11·4%) (compare Francis and Willson, *loc. cit.*). The aqueous liquid, on treatment with semicarbazide acetate, yielded the semicarbazone of the same ketone; m. p. 224° (Found: C, 60·7; H, 9·6. Calc.: C, 60·9; H, 9·6%) (compare Francis and Willson).

1 - *Bromo* - 2 : 2 : 3 : 3 - *tetramethyl* - [0,1,2] - dicyclo*pentan* - 4 - *ol*-5-*one* (1-*Bromo*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-5-*ol*-4-*one*).—This compound (yield nearly quantitative; m. p. 116°. Found: C, 46·4; H, 5·6. Calc.: C, 46·3; H, 5·6%), its acetyl derivative (m. p. 74°. Found: C, 48·2; H, 5·6. Calc.: C, 48·0; H, 5·5%), and benzoyl derivative (m. p. 92°. Found: C, 56·8; H, 5·3. Calc.: C, 57·0; H, 5·0%), we have prepared by the methods of Francis and Willson. The free hydroxy-compound gives a wine-red colour with aqueous-alcoholic ferric chloride. Since the benzoyl derivative provides the most convenient route to the reduced compounds mentioned below, the following details of its preparation may be given. The hydroxy-compound (12 g.) and benzoyl chloride (8 g.) were heated in pyridine solution on the steam-bath for 30 minutes. The ethereal extract obtained after the mixture had been poured into water was washed several times with dilute sulphuric acid and

with dilute sodium hydroxide solution, dried with calcium chloride, and evaporated. The solid residue was crystallised twice from aqueous alcohol, and obtained as colourless needles, m. p. 92°. Neither the acyl derivatives nor the hydroxy-compound appears to yield an oxime or semicarbazone. The *d-bromocamphor-sulphonyl* derivative was prepared by boiling a xylene solution of *d*-bromocamphorsulphonyl chloride with the silver derivative of the bromohydroxy-compound. After distillation of the xylene, the product was extracted with ether and the extract was washed with aqueous sodium carbonate, dried, and evaporated. The residue crystallised from ligroin or alcohol in pearly plates, m. p. 150° (Found: C, 43·2; H, 5·2. $C_{19}H_{26}O_5Br_2S$ requires C, 43·3; H, 5·0%). The compound decolorises permanganate in cold acetone with moderate rapidity, and does not appear to be capable of separation into optical isomerides by fractional crystallisation.

The *methyl* derivative was prepared by the action of an excess of methyl iodide on the solution obtained by adding the bromohydroxy-compound to an exact equivalent of alcoholic sodium ethoxide. After heating for 1 hour on the steam-bath, the mixture was poured into water and extracted with ether. The extract was washed with water, dilute sodium hydroxide solution and water, dried with calcium chloride, and evaporated. Distillation yielded the product as a colourless oil, which gave no colour with aqueous alcoholic ferric chloride. As it did not appear to form an oxime or semicarbazone, we have not been able to characterise it by means of crystalline derivatives, and there is therefore no proof that it is not a mixture of isomerides. If this is the case, however, the principal constituent is an unsaturated *O*-methyl ether, because the oil readily reduces cold permanganate in the presence of sodium hydrogen carbonate in aqueous acetone, and on hydrolysis by hydriodic acid yields the original bromohydroxy-compound. The refractive indices of different preparations do not agree very closely: $n_D^{20-21^\circ}$ 1·5131—1·5147; the following densities have been observed: $d_{4^\circ}^{17^\circ}$ 1·3203, $d_{4^\circ}^{20^\circ}$ 1·3159, $d_{4^\circ}^{21^\circ}$ 1·3162; and the following uncorrected b. p.'s: 95°/3 mm., 120°/14 mm., 130°/20 mm., 133°/25 mm. (Found: C, 48·3; H, 5·9. $C_{10}H_{15}O_2Br$ requires C, 48·6; H, 6·1%). A substance having substantially identical properties can be obtained, but less satisfactorily, by methylating the bromohydroxy-compound with twice the theoretical amount of methyl sulphate and excess of aqueous sodium hydroxide. The mixture was heated on the steam-bath for 1 hour, poured into water, and extracted with ether. A third method consists in allowing the silver salt of the bromohydroxy-compound to react with excess of methyl iodide in the cold; $d_{4^\circ}^{20^\circ}$ 1·3167; $n_D^{20^\circ}$ 1·5148.

The p-*bromobenzyl* derivative was prepared by means of *p*-bromobenzyl bromide and alcoholic sodium ethoxide, the mixture being heated on the steam-bath for 2 hours before being worked up as in the preceding example. The residue from the ethereal extract readily solidified and on crystallisation from dilute alcohol yielded iridescent plates, m. p. 65° (Found: C, 47·8; H, 4·4. $C_{16}H_{18}O_2Br_2$ requires C, 47·8; H, 4·5%). The same compound is obtained by allowing *p*-bromohenzyl bromide to react with the silver derivative of the bromohydroxy-compound in boiling ethereal-alcoholic solution. It forms no semicarbazone and does not give a colour with aqueous-alcoholic ferric chloride. It does not attack bromine in chloroform, does not form a semicarbazone, and is remarkably stable to dilute alkaline permanganate in aqueous acetone even at 65—70°. Part of the product of the action of *p*-bromobenzyl bromide on the sodio-derivative is an uncrystallisable oil, which is obtained from the ultimate mother-liquors in the crystallisation. It reduces permanganate but does not give a colour with ferric chloride; its behaviour on reduction is described below.

The p-*nitrobenzyl* derivative, similarly prepared, crystallises from alcohol in pearly plates, m. p. 111° (Found: C, 52·2; H, 5·1. $C_{16}H_{18}O_4NBr$ requires C, 52·2; H, 4·9%).

1-*Cyano*-2 : 2 : 3 : 3-*tetramethyl*-[0,1,2]-dicyclo*pentan*-4-*ol*-5-*one* (1-*Cyano*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-5-*ol*-4-*one*).—This substance was obtained in poor yield both by heating the bromohydroxy-compound in 50% alcoholic solution containing an excess of potassium cyanide on the steam-bath for 3 hours, and by boiling a solution of the bromohydroxy-compound in ligroin (b. p. 100—120°) with silver cyanide for 6 hours. After several crystallisations from ligroin, it was obtained as colourless needles, m. p. 172—173° (Found: N, 8·0. $C_{10}H_{13}O_2N$ requires N, 7·8%).

2 : 2 : 3 : 3-*Tetramethyl*-[0,1,2]-dicyclo*pentan*-4-*ol*-5-*one* (2 : 2 : 3 : 3-*Tetramethyl*-Δ^5-cyclo*penten*-5-*ol*-4-*one*).—This was prepared, as described by Francis and Willson, both by reduction of the bromohydroxy-compound with zinc dust and glacial acetic acid, and by reduction of the bromoacetoxy-derivative with the same reagents and subsequent saponification with aqueous sodium hydroxide. Even by the latter method, however, we were unable to obtain more than an approximately 70% yield (contrast Francis and Willson), owing, as it subsequently appeared, to the fact that under our conditions part of the unsaturated halogen-free acetoxy-compound undergoes further reduction to a dihydro-derivative (*vide infra*). The free hydroxy-compound gives a dull red colour with aqueous alcoholic ferric chloride. The *acetyl* derivative, when purified by distillation after preparation in the manner indicated, or when

prepared by acetylation of the halogen-free crystalline hydroxy-compound by boiling for 1 hour with excess of acetic anhydride, is a colourless oil, b. p. 120°/15—16 mm. (Found: C, 67·0; H, 8·7. $C_{11}H_{16}O_3$ requires C, 67·2; H, 8·2%). It readily absorbs bromine in chloroform, and decolorises a cold aqueous acetone solution of potassium permanganate and sodium hydrogen carbonate; it gives no colour with aqueous-alcoholic ferric chloride. For the density and refractive index we find $d_4^{20^\circ}$ 1·0190 and $n_D^{20^\circ}$ 1·4549, whence $[R_L]_D = 52{\cdot}21$. The exaltations given on p. 384 are calculated from Eisenlohr's (1910) constants. The benzoyl compound was prepared by Francis and Willson by benzoylation of the hydroxy-derivative. We have prepared it in considerable quantities by reducing the bromobenzoyloxy-compound with half its weight of zinc dust in boiling glacial acetic acid for about 2·5 hours. The mixture is then cooled, the liquid decanted from the zinc and zinc acetate into water, the solid washed with fresh acetic acid, and the precipitated oil extracted with ether. The extract was washed with cold 10% sodium hydroxide solution, dried, and evaporated. The product separates from dilute alcohol in glistening plates, m. p. 68° (after two crystallisations), and is identical with the material prepared by Francis and Willson's method (Found: C, 74·25; H, 7·1. Calc.: C, 74·4; H, 7·0%). It gives no colour with aqueous-alcoholic ferric chloride, and permanganate in aqueous acetone containing sodium hydrogen carbonate remains coloured for many hours. It is also unaffected by bromine in chloroform, and does not appear to undergo further reduction by prolonged treatment with excess of zinc dust in boiling glacial acetic acid. It is not easily hydrolysed by aqueous sodium hydroxide, but hydrolysis can be effected by heating on the steam-bath for 1 hour with 10% aqueous-alcoholic potassium hydroxide. The mixture is then evaporated to expel most of the alcohol, acidified, and extracted with ether, and the benzoic acid is removed from the ethereal solution by washing with aqueous sodium hydrogen carbonate. This provides the most satisfactory method for the preparation of the free hydroxy-compound.

The *methyl* derivative has been prepared by the following three methods: (1) The halogen-free hydroxy-compound was warmed on the steam-bath for 2 hours with methyl sulphate and 10% aqueous sodium hydroxide. After decomposition of the excess of methyl sulphate the methylation product was extracted with ether. In one experiment we obtained an oil, which, on strong cooling, yielded well-formed needles, m. p. 37° (Found: C, 71·2; H, 9·6. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%). The quantity obtained was small and was almost all used for the analysis. Unfortunately,

despite many attempts, we have not since succeeded in reproducing this result, and are therefore unable to describe the properties of this solid derivative. On all other occasions the product has been a colourless oil, b. p. 112—115°/21 mm., $n_D^{19°}$ 1·4687 (Found: C, 70·2; H, 9·3; OMe, 18·1. Calc.: OMe, 18·5%), which rapidly decolorises cold alkaline permanganate, and absorbs bromine in chloroform. It gives no colour with ferric chloride. (2) The hydroxy-compound was heated for 2 hours on the steam-bath with a methyl-alcoholic solution of sodium methoxide (1 mol.) and excess of methyl iodide. The product was poured into water and extracted with ether, and the extract dried and distilled. The distillate, b. p. 108—112°/18 mm., $n_D^{19°}$ 1·4687, OMe 18·1%, has properties identical with those of the product obtained by method (1). (3) The bromomethoxy-compound was reduced by the method already described for the reduction of the bromoacetoxy-compound. The methoxy-compound so obtained was purified by distillation, controlled by b. p. and refractive-index determinations (*vide* the dihydro-derivative). Since the liquid methoxy-compound gives an oily oxime, and we have not been able to prepare a crystalline derivative, there is no proof that it is not a mixture of isomerides; but if this is so, the principal constituent is 5-methoxy-2 : 2 : 3 : 3-tetramethyl-Δ^5-*cyclo*penten-4-one, as is shown by its behaviour on further reduction (below). The Zeisel determinations show that it cannot contain a substantial proportion of any *C*-methylation product. The oxime has b. p. 140—150°/22 mm.

The p-*bromobenzyl* derivative was prepared by reducing the bromo-*p*-bromobenzyloxy-compound with glacial acetic acid and excess of zinc. After boiling for 3 hours, the acetic acid solution was poured into water and extracted with ether. The ethereal extract was washed with cold alkali, dried, and evaporated. The crystalline residue separated from ligroin in long, colourless prisms, m. p. 86° (Found: C, 59·2; H, 5·9. $C_{16}H_{19}O_2Br$ requires C, 59·3; H, 5·9%). The same substance was obtained by heating the hydroxy-compound (1·0 g.) with methyl-alcoholic sodium methoxide (prepared from 0·16 g. of sodium) and *p*-bromobenzyl bromide (1·7 g.) on the steam-bath for 1 hour (yield, 90%). The compound gives no colour with aqueous-alcoholic ferric chloride. It slowly decolorises permanganate in acetone, and does not appear to absorb bromine in cold chloroform, although on warming bromine disappears and hydrogen bromide is evolved, showing that substitution has taken place. It forms a crystalline oxime (p. 403).

3 : 3 : 4 : 4-*Tetramethyl*cyclo*pentanone*.—Francis and Willson obtained this substance from the bromohydroxy-compound by reduction with sodium amalgam, which is a convenient reagent for

the preparation of small quantities. For larger amounts the Clemmensen method is preferable. The reduction is complete in 1 hour and the ketone is then removed from the water-cooled trap employed to collect it. A further small quantity is obtainable from hydrochloric acid solution by distillation in steam (total yield, 75%). We have also prepared the ketone by the action of sodium amalgam on a hot aqueous solution of the bromine-free hydroxy-compound, and by the action of hydriodic acid at 140° on its methyl and *p*-bromobenzyl derivatives, as well as by the methods described elsewhere in this paper.

The *dipiperonylidene* derivative was obtained by boiling under reflux a solution of the ketone (0·5 g.), piperonaldehyde (1·5 g.), and potassium hydroxide (1·5 g.) in 80% alcohol (30 c.c.) for 1 hour. The cooled solution was diluted with water, and the product, which was precipitated as a slowly solidifying oil, was drained, washed with ligroin, and crystallised from methyl alcohol, from which it separated in yellow, rhombic prisms, m. p. 125° (Found : C, 74·0; H, 6·0. $C_{25}H_{24}O_5$ requires C, 74·2; H, 6·0%).

The *αα'-dioximino*-derivative (1 : 3-*dioxime* of 4 : 4 : 5 : 5-tetramethyl*cyclo*pentanetrione) was prepared by treating the ketone (0·7 g.) with *iso*amyl nitrite (1·2 g.) in ethyl alcohol (1·0 c.c.) containing 10 drops of concentrated hydrochloric acid. After being kept for 30 minutes, during which the temperature rose to 40°, the solution was basified with sodium hydroxide and extracted with ether, then acidified, and again extracted with ether. The second extract was washed with sodium hydrogen carbonate solution, dried, and evaporated, and the residue was washed with ether and chloroform (yield, 60%). The same substance was obtained from the ketone (0·7 g.), *iso*amyl nitrite (1·2 g.), and 0·5 c.c. of a solution of sodium methoxide prepared by dissolving 0·12 g. of sodium in 2 c.c. of methyl alcohol. The mixture was kept at 40° for 20 minutes, cooled, diluted with water, mixed with aqueous sodium hydroxide, and extracted with ether. The aqueous solution was then saturated with carbon dioxide and again extracted. Another method which has been used consists in passing nitrosyl chloride into a solution of the ketone in chloroform, ether, or ligroin. The dioxime separates from alcohol in pale yellow needles, m. p. 223° (decomp.) (Found : C, 54·1; H, 7·0. $C_9H_{14}O_3N_2$ requires C, 54·5; H, 7·1%). On hydrolysis with hydrochloric acid in the presence of formaldehyde (Perkin's method) it yielded a nitrogen-free oil which reduced Fehling's solution and stained the skin purple just as does 1 : 2 : 3-triketohydrindene. This evidently consisted of tetramethyl*cyclo*pentanetrione or its hydrate, since on treatment with excess of hydroxylamine acetate in boiling 90% alcohol, it was converted

into a crystalline 1 : 2 : 3-*trioxime*, which was isolated by evaporating the alcohol and extracting the residue with chloroform. The same trioxime was obtained directly from the 1 : 3-dioxime by treatment with hydroxylamine acetate under the conditions described. It separates from chloroform–ether in colourless needles, m. p. 168—169° (Found : N, 19·5. $C_9H_{15}O_3N_3$ requires N, 19·7%), and gives a strong purple colour with aqueous-alcoholic ferric chloride.

The oxime was prepared by heating tetramethyl*cyclo*pentanone with an excess of aqueous-alcoholic hydroxylamine acetate for some hours on the steam-bath. The partly evaporated solution was extracted with ether, and the dried and concentrated ethereal solution was treated with dry hydrogen chloride, which precipitated the *hydrochloride* of the oxime, m. p. 119° (Found : Cl, 18·4. $C_9H_{17}ON,HCl$ requires Cl, 18·5%). The solution of this in aqueous sodium carbonate yielded the pure *oxime*, m. p. 107°, on extraction with ether (Found : N, 9·1. $C_9H_{17}ON$ requires N, 9·0%). The oxime is very soluble in most organic solvents, but can be crystallised from ligroin. It is volatile in steam. It reduces Fehling's solution and gives a green colour with bromine in aqueous pyridine (Piloty, *Ber.*, 1898, **31**, 454).

Formation of 3 : 3 : 4 : 4-*Tetramethyl*cyclo*pentanone from Pinacol and Ethyl Acetonedicarboxylate.*—Pinacol was converted into βγ-dibromo-βγ-dimethylbutane (m. p. 173°; compare Centurier, *Ann. Chim. Phys.*, 1892, **26**, 444) by treatment with the theoretical amount of phosphorus tribromide. Ethyl acetonedicarboxylate (20·2 g.), the dibromide (24·4 g.), and alcoholic sodium ethoxide prepared from 4·6 g. of sodium and 50 g. of ethyl alcohol were heated together for 4 hours on the steam-bath. The product was worked up into fractions insoluble in alkali, insoluble in sodium hydrogen carbonate hut soluble in sodium hydroxide, and soluble in carbonate, but difficulty was experienced in the purification of these, and they were therefore hydrolysed by boiling with 20% hydrochloric acid under an efficient condenser. On distillation in steam the eliminated alcohol and the ketone passed over in the first runnings, from which the ketone was collected in the form of its semicarbazone, m. p. 224°, after addition of semicarbazide acetate.

Conversion of 3 : 3 : 4 : 4-*Tetramethyl*cyclo*pentanone into the Bromo-hydroxy-compound.*—A general description of these experiments is given in the introduction (p. 369), and it need be added only that the product was identified by m. p., mixed m. p., and analysis, and by the m. p. and mixed m. p. of its acetyl derivative.

3 : 3 : 4 : 4-*Tetramethyl*cyclo*pentylamine.*—(1) A solution of 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone oxime (2·0 g.) in alcohol was heated to 50—60° while 2·5% sodium amalgam (50 g.) and hot

glacial acetic acid were gradually added. The solution was cooled, separated from the mercury, diluted with water, and extracted with ether to remove any unchanged oxime. After basification with sodium hydroxide, the amine was extracted with ether, and the extract was dried with potassium carbonate and distilled through a fractionating column.

(2) A boiling solution of the oxime (2·0 g.) in absolute alcohol (50 g.) was slowly poured on sodium wire (5 g.), contained in a flask fitted with an efficient reflux condenser. After addition of an excess of aqueous acetic acid, the solution was evaporated to drive off most of the alcohol, extracted with ether, basified, and again extracted, the ether being finally removed through a column.

(3) The oxime (1·0 g.) was first converted into its acetyl derivative by mixing a solution in dry pyridine with acetyl chloride (0·5 g.) with external cooling. The product was isolated by pouring into dilute sulphuric acid and extracted with ether. The extract, after being washed with dilute acid, dried, and evaporated, gave a colourless oil, which yielded no precipitate when its solution in dry ether was treated with dry hydrogen chloride. The acetate was dissolved in 75 c.c. of glacial acetic acid, and treated with 10 g. of palladised barium sulphate (corresponding to 0·5 g. of palladium), and hydrogen at the ordinary temperature and 1·5 atmospheres pressure, with shaking, until the requisite amount of hydrogen had been absorbed (usually less than 1 hour). The mixture was then decanted into water, and the precipitate washed by decantation with fresh acetic acid; the diluted acid solution was then extracted with ether, basified with sodium hydroxide, and again extracted, the second extract yielding the amine.

The base obtained by these methods forms colourless needles, m. p. 100—102°, having a characteristic odour. Owing to its volatility, and great solubility in the usual solvents, we did not recrystallise it, but characterised it by means of its salts and acetyl derivative. The *picrate* was precipitated in alcoholic solution and crystallised twice from alcohol, from which it separated in bright yellow needles, m. p. 255° (decomp.) (Found: C, 48·1; H, 6·0. $C_{15}H_{22}O_7N_4$ requires C, 48·6; H, 6·0%). The *chloroaurate*, obtained by addition of chloroauric acid to a hydrochloric acid solution of the base, separated from 15% hydrochloric acid in orange-yellow needles, m. p. 230° (decomp.) (Found: C, 22·6; H, 4·6; Au, 39·9. $C_9H_{20}NCl_4Au$ requires C, 22·4; H, 4·2; Au, 40·1%). The *hydrochloride*, precipitated from ethereal solution by dry hydrogen chloride, had m. p. 308° (decomp.) and was very deliquescent. The *acetyl* derivative was prepared by boiling the picrate (0·5 g.) for 2 hours with excess of acetic anhydride in the presence of

anhydrous sodium acetate (0·5 g.). The product was poured into water, and, after decomposition of the acetic anhydride, extracted with ether. The acetic acid and picric acid were removed by washing with 5% aqueous sodium hydroxide, and the extract was dried with potassium carbonate and evaporated. The oil solidified while still hot (yield, 0·20 g.; m. p. 95°, unpurified), and crystallisation from ligroin yielded felted needles, m. p. 95° (Found: C, 71·9; H, 11·4. $C_{11}H_{21}ON$ requires C, 72·1; H, 11·4%).

2 : 2 : 3 : 3-*Tetramethyl*-[0,1,2]-dicyclo*pentan*-4-*ol*-5-*one Oximes*.—A solution of the hydroxy-ketone (0·5 g.), hydroxylamine hydrochloride (0·23 g.), and sodium acetate (0·27 g.) in 3 c.c. of 10% aqueous sodium hydroxide was kept at 40° for 40 hours; the precipitate was then collected, and washed with a little water, alcohol, and ether. This substance, m. p. 200° (decomp.), contained sodium and was evidently the *sodium* salt of an oxime. Its solution in water, on treatment with carbon dioxide, yielded the *monohydrate* of the α-oxime, m. p. 75°, as pearly plates, which after a further crystallisation from water had m. p. 76—77° (Found: H_2O, 9·6. $C_9H_{15}O_2N,H_2O$ requires H_2O, 9·7%). On desiccation in a vacuum the hydrate became converted into the anhydrous *α-oxime*, m. p. 96° (Found: N, 8·5. $C_9H_{15}O_2N$ requires N, 8·3%), which crystallised from carbon tetrachloride–ligroin in long prisms having the same m. p. The filtrate from the oxime hydrate was acidified with hydrochloric acid at 0° and extracted with ether; a gum was then obtained which, on desiccation, set to a slowly crystallising glass. On crystallisation from carbon tetrachloride–ligroin, this yielded pearly leaflets, m. p. 174—175°, which gave the reactions of a hydrochloride and contained solvent of crystallisation. On heating at 100° a loss in weight amounting to 38% (theory for 1 mol. of CCl_4, 43%) occurred, and the product then had m. p. 189—190° (Found: C, 53·5; H, 8·2. $C_9H_{16}O_2NCl$ requires C, 52·5; H, 8·2%). This is apparently the *hydrochloride* of the α-oxime, since its solution in water is acid, contains chloride ions, and on basification yields the α-oxime. This was obtained by extraction with ether after addition of sodium carbonate, and dehydration in ethereal solution with anhydrous potassium carbonate. The product was identified with the oxime, m. p. 96° (mixed m. p.), and then crystallised from water, the monohydrate, m. p. 76—77°, being obtained. The carbon tetrachloride–ligroin mother-liquors, on concentration, deposited crystals of the same oxime hydrate. In another experiment in which 5 g. of the hydroxy-ketone were condensed with hydroxylamine acetate, precipitation of the sodium salt of the oxime did not occur, and the whole yield of oxime was isolated by way of the hydrochloride in the manner indicated by the preliminary

investigation described. The *benzoyl* derivative of the oxime crystallised from dilute alcohol in colourless needles, m. p. 134—135° (Found: C, 70·0; H, 7·4. $C_{16}H_{19}O_3N$ requires C, 70·3; H, 7·0%).

When the α-oxime is treated with dry hydrogen chloride in cold ethereal solution, a new *hydrochloride*, m. p. 69—70°, is precipitated. On basification of its solution with sodium carbonate the hydrate of the α-oxime is precipitated, and the mother-liquors on concentration yield further crops of the same substance. However, on desiccation in a vacuum over potassium hydroxide the β-hydrochloride loses hydrogen chloride and gives the *β-oxime*, m. p. 114—115°, which on crystallisation from chloroform–ligroin forms rhombic prisms, m. p. 115° (Found: C, 64·1; H, 9·1. $C_9H_{15}O_2N$ requires C 63·9; H, 8·9%). On two occasions the β-oxime was obtained directly from the hydroxy-ketone and hydroxylamine, but we have not determined the exact conditions in which it is produced in place of the α-oxime. The second of these experiments was conducted as follows. A solution of the hydroxy-ketone (1 mol.), hydroxylamine hydrochloride (1 mol.), and sodium acetate (excess) in aqueous methyl alcohol was warmed at 40° for a short time and kept overnight. The solution was then made strongly acid with 15% hydrochloric acid, extracted with ether to remove the unchanged ketone, carefully neutralised with sodium hydrogen carbonate, made alkaline with sodium carbonate (1 mol.), and immediately extracted with ether. The residue from the ether was an oil, which solidified on rubbing, and after being washed with ligroin and crystallised, was identified as the β-oxime, m. p. 115°.

On boiling with water the β-oxime is converted into the hydrate of the α-oxime. A mixture of the α- and β-oximes melted at about 60°. Both oximes reduce Fehling's solution, but the α-oxime forms no colour with ferric chloride, whereas the β-oxime gives a red-purple colour.

When the β-hydrochloride was treated with hydrogen chloride in boiling ethereal solution, a red oil was obtained which subsequently solidified. The drained crystals were crystallised first from carbon tetrachloride–ligroin, and then from water (charcoal) which removed the red colour and yielded needles, m. p. 113° (a mixture with the β-oxime melted below 80°) (Found: C, 63·7; H, 8·9. $C_9H_{15}O_2N$ requires C, 63·9; H, 8·9%). The substance is not soluble in cold aqueous sodium carbonate, but in 10% potassium hydroxide it forms a pale yellow solution which, on acidification, becomes colourless. On account of its non-identity with ααββ-tetramethylglutarimide, we provisionally assign to this substance the formula of the *lactam* of *δ-amino-α-keto-ββγγ-tetramethylvaleric acid.*

ααββ-*Tetramethylglutaric anhydride*, which was prepared from the acid and acetic anhydride in the usual way, has m. p. 184°. On heating in a stream of dry gaseous ammonia, it is converted into the *imide*, which after sublimation has m. p. 200—202° (Found: N, 8·8. $C_9H_{15}O_2N$ requires N, 8·3%). The imide gives no colour with ferric chloride.

The hydroxy-ketone, or its α-monoxime, m. p. 96°, was heated for 2 hours on the steam-bath in ethyl-alcoholic solution with an excess of hydroxylamine hydrochloride, and anhydrous sodium acetate. The solution was filtered while hot, and mixed with ice-cold water, and the precipitated *dioxime* of 3 : 3 : 4 : 4-*tetramethyl*cyclo*pentane*-1 : 2-*dione* purified by crystallisation from dilute alcohol. It forms rhombic prisms, m. p. 211° (decomp.) (Found: C, 58·8; H, 8·6. $C_9H_{16}O_2N_2$ requires C, 58·7; H, 8·8%). Its formulation as a 1 : 2-dioxime was confirmed by conversion into the furazan. For this purpose, the dioxime (0·5 g.) was heated with 3 c.c. of concentrated aqueous ammonia in a closed tube at 160—170° for 5 hours. The *furazan*, which crystallised on cooling, was dried and crystallised from a large volume of ligroin (b. p. 100—120°), from which it separated in flattened prisms, m. p. 209° (Found: C, 64·9; H, 8·8. $C_9H_{14}ON_2$ requires C, 65·0; H, 8·5%). The furazan is insoluble in cold 10% aqueous potassium hydroxide. The same dioxime and furazan can be prepared by starting with the α-oxime, m. p. 96°, in place of the hydroxy-ketone.

The hydroxy-ketone and *o*-phenylenediamine in equimolecular proportion were boiled in glacial acetic acid solution. The *condensation product*, which separated, after cooling, on addition of water, crystallised from dilute alcohol in golden-yellow needles, m. p. 100° (Found: C, 78·8; H, 8·1. $C_{15}H_{18}N_2$ requires C, 79·5; H, 8·0%).

The *semicarbazone* of the hydroxy-ketone was prepared by the usual method; it crystallised from dilute alcohol in colourless plates, m. p. 211—213° (decomp.) (Found: C, 56·8; H, 8·4. $C_{10}H_{17}O_2N_3$ requires C, 56·9; H, 8·1%).

The *anil* of the hydroxy-ketone, which was obtained by heating the latter (0·5 g.) with aniline (0·3 g.) at 100° for 1 hour, separated from ligroin in rhombic prisms, m. p. 104° (Found: C, 78·3; H, 8·4. $C_{15}H_{19}ON$ requires C, 78·6; H, 8·4%). The p-*dimethylaminoanil*, similarly prepared and purified, formed yellow needles, m. p. 90° (Found: C, 75·4; H, 8·8. $C_{17}H_{24}ON_2$ requires C, 75·0; H, 8·8%). These anils do not react easily with hydroxylamine, but when heated for 30 hours in alcoholic solution with hydroxylamine hydrochloride (6 mols.) and anhydrous sodium acetate (excess), yield the dioxime, m. p. 211° and unidentified substances.

Reduction of the α-Oxime (*m. p.* 96°) *to* 3 : 3 : 4 : 4-*Tetramethyl*cyclo*pentylamine*.—This was effected by the three methods mentioned on p. 392, the oxime being acetylated before reduction by method 3. The identity of the base with that obtained from 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone oxime (m. p. 107°) was established by the following comparisons of m. p.'s and mixed m. p.'s :—

	Base.	Picrate.	Dichloro-aurate.	Hydro-chloride.	Acetyl derivative.
From 96°-oxime ...	100—102°	254°	229°	305°	94°
„ 107°-oxime ...	100—102	255	230	308	95
Mixed m. p.	100—102	254—255	229—230	306	94

Reduction of the Acetyl Derivative of the Hydroxy-ketone.—A boiling solution of the acetyl derivative (7·5 g.) in glacial acetic acid (100 c.c.) was treated with 10 g. of zinc dust, which was added gradually during 6 hours. The cooled solution was filtered, the solid residue washed by decantation with fresh acetic acid, and the combined filtrates mixed with water and extracted with ether. The extract was washed with aqueous sodium carbonate solution, dried, and evaporated. The oily residue on fractional distillation yielded a small quantity of unchanged substance (b. p. 120°/15—16 mm.; 1·2 g.) and a main fraction (3·4 g.), b. p. 127°/15—16 mm. This substance is shown in the sequel to be 5-*acetoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone* (Found : C, 66·2; H, 9·3. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·2%). On hydrolysis it gives a hydroxy-ketone, $C_9H_{16}O_2$, m. p. 140°, which is being investigated. These substances are more conveniently prepared directly from the acetyl derivative (m. p. 74°) of the bromohydroxy-compound by reduction under the conditions described above.

2 : 2 : 3 : 3-*Tetramethyl*cyclo*pentanone*.—A boiling glacial acetic acid solution of the acetoxytetramethyl*cyclo*pentanone was treated during 0·5 hour with 100 g. of 2·5% sodium amalgam. The cooled and diluted solution was extracted with ether, and the extract washed with dilute sodium carbonate solution, dried, and distilled (column). The oily residue, which had a strong odour resembling that of camphor, was distilled; 2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone* was then obtained as a wax-like solid, b. p. 100°/16 mm., m. p. 119° (mixed m. p. with 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone, 105°), together with a less volatile fraction, b. p. 127°/16 mm., consisting of the unaltered acetoxy-ketone. The 2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone obtained by this method is liable to be contaminated with traces of the 3 : 3 : 4 : 4-isomeride, which may be removed by taking advantage of the fact that it combines with semicarbazide much more rapidly than the 2 : 2 : 3 : 3-compound. For this purpose the crude ketone is treated with aqueous-alcoholic semi-

carbazide acetate at 18° for 30 minutes, and any precipitate which is formed is removed by filtration. From this the semicarbazide of the 3 : 3 : 4 : 4-ketone has been isolated by crystallisation. The 2 : 2 : 3 : 3-ketone is recovered from the filtrate by largely diluting it and extracting it with ether, and is finally purified by distillation. For the preparation of 2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone in quantity it is convenient to employ, in place of the saturated acetoxy-ketone, the mixture of reduction products obtained by the action of zinc and acetic acid on the bromoacetoxy-compound, the precaution being taken of removing any 3 : 3 : 4 : 4-ketone in the manner described. It is also possible to obtain the ketone directly from the bromoacetoxy-compound by reduction with glacial acetic acid and a larger proportion of sodium amalgam.

The *semicarbazone* separates in the course of 24 hours when the ketone is left in contact with aqueous-alcoholic semicarbazide acetate at the ordinary temperature. It crystallises from dilute alcohol in needles, m. p. 222° (decomp.) (mixed m. p. with the semicarbazone, m. p. 224°, of 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone, 200—205°) (Found: C, 60·9; H, 9·9. $C_{10}H_{19}ON_3$ requires C, 60·9; H, 9·6%).

The *oxime* was prepared by boiling an alcoholic solution of the ketone for 18 hours with a slight excess of hydroxylamine hydrochloride and anhydrous sodium acetate. After dilution with water, the oxime was extracted with ether, and the extract washed with aqueous sodium carbonate, dried with calcium chloride, and concentrated to a small bulk. Dry hydrogen chloride was then passed in, and the *oxime hydrochloride*, m. p. 125° (Found: Cl, 18·6. $C_9H_{17}ON,HCl$ requires Cl, 18·5%), collected and washed with ether. The free oxime, liberated by means of sodium carbonate and isolated by extraction with ether, had m. p. 101—102°. It is extremely soluble in the usual organic solvents.

2 : 2 : 3 : 3-*Tetramethyl*cyclo*pentylamine*.—This was prepared from the oxime by reduction with sodium and alcohol as described on p. 392. The base is crystalline (needles) at the ordinary temperature, and is closely similar in odour and volatility to 3 : 3 : 4 : 4-tetramethyl*cyclo*pentylamine; but, apart from noting these points, we have not investigated the free amine owing to the rapidity with which it disappears. Its *picrate* separates from methyl alcohol–ligroin in yellow needles, m. p. 242—243° (decomp.). Found: C, 48·9; H, 5·9. $C_{15}H_{22}O_7N_4$ requires C, 48·6; H, 6·0%). It is closely similar in appearance to the picrate (m. p. 255°) of the isomeric base, but a mixture of the two melted at 235—236°. The *acetyl* derivative, obtained from the picrate by boiling with acetic anhydride and sodium acetate, separated from ligroin in prisms, m. p. 115° (Found;

C, 71·9; H, 11·4. $C_{11}H_{21}ON$ requires C, 72·1; H, 11·4%). A mixture with the acetyl derivative of the isomeric base had m. p. 83—85°.

*Reduction of the Oxime of 5-Acetoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone.*—The oxime was prepared in the usual way, but it could not be crystallised and therefore was reduced, without purification, by means of sodium and alcohol. The product was identified as 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine.

Action of Hydroxylamine on the Benzoyl Derivative of the Hydroxy-ketone.—(1) The benzoyloxy-compound was dissolved in a cold ethyl-alcoholic solution of hydroxylamine hydrochloride (1 mol.) containing dry sodium hydrogen carbonate (1 mol.) in suspension. After being kept at the ordinary temperature for 18 hours, the product was poured into water and extracted with ether, and the extract was washed with dilute sodium carbonate solution, dried, and evaporated. The *oxime* thus obtained in excellent yield separated from hot water or from chloroform–ligroin in well-developed prisms, m. p. 115° (Found : C, 63·8; H, 8·8. $C_9H_{15}O_2N$ requires C, 63·9; H, 8·9%). The sodium carbonate solution on acidification yielded benzoic acid. The new oxime, which may be distinguished by the prefix γ-, gives a pale red-brown colour with ferric chloride. It is soluble in sodium hydroxide and concentrated hydrochloric acid, and can be recovered from each solution unchanged, in the former case by neutralisation, and in the latter by dilution. A mixture with the β-oxime (m. p. 115°), described on p. 395, melted at about 100°, and a mixture with the isomeric lactam (m. p. 113°) (p. 395) melted at 85°. The same oxime was obtained by various modifications of the method described above, as, for instance, heating an alcoholic solution of the hydroxy-ketone with anhydrous sodium acetate (excess) and hydroxylamine hydrochloride (1 mol.) for 3 hours on the steam-bath. On boiling with dilute hydrochloric acid, the oxime is hydrolysed to the original hydroxy-ketone, which may crystallise from the solution on cooling or can be extracted with ether. When, however, hot concentrated hydrochloric acid is used in attempted hydrolysis, deep-seated changes take place and an intractable oil is produced.

(2) An alcoholic solution of the benzoyloxy-compound (2·5 g.) was boiled for 2 hours with hydroxylamine hydrochloride (3·5 g.) and anhydrous sodium acetate (4·0 g.). On working up the product, as in the preceding experiment, the dioxime, m. p. 211° (decomp.), was obtained together with benzoic acid. The same dioxime is obtained when the monoxime is further oximated under the same conditions.

Re-arrangement of the γ-Oxime.—The monoxime was heated in

a closed tube at 100° for 30 minutes with a chloroform solution of nitrosyl chloride. On evaporation an oil remained which soon became semi-solid. The crystals were drained, washed with ligroin and with xylene, and crystallised from carbon tetrachloride–ligroin, from which colourless octahedra separated, m. p. 200° (Found: C, 63·5; H, 8·5. $C_9H_{15}O_2N$ requires C, 63·9; H, 8·9%). The substance is soluble in cold 10% potassium hydroxide solution, and gives a faint red colour with ferric chloride. It is provisionally regarded as the *lactam* of *δ-amino-α-keto-γγ-dimethyl*iso*heptoic acid*.

Reduction of the γ-Oxime.—The oxime was reduced with excess of sodium in boiling alcohol, as described on p. 392, and the base isolated and converted into its picrate. The latter was much more soluble in alcohol than the picrates of the tetramethyl*cyclo*pentylamines, and was therefore precipitated from ethereal solution. In the crude state it had m. p. 220—221°, and separated from alcohol–ligroin in yellow needles, m. p. 221° (Found: C, 46·8, 46·9; H, 5·7, 5·8; N, 14·9. $C_{15}H_{22}O_8N_4$ requires C, 46·6; H, 5·7; N, 14·5%). The substance thus appears to be the *picrate* of *5-hydroxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine*.

*Action of Amyl Nitrite and Sodium Methoxide on 3 : 3 : 4 : 4-Tetramethyl*cyclo*pentanone.*—Unless special precautions are taken, the sole product obtained from the reaction indicated is the αα'-dioximino-compound described on p. 391. By carefully regulating the conditions, however, we have obtained, although in very small yield, a mono-oximino-derivative which appears to be identical with the γ-oxime obtained from the benzoyloxy-compound (above). The ketone (6 g.) and *iso*amyl nitrite (5 g.) were mixed at 0° with a solution of sodium methoxide prepared from 0·12 g. of sodium and 2 c.c. of methyl alcohol. The mixture was slowly warmed to 35—38° and maintained at this temperature for 20—30 minutes. (The limiting conditions of success in this experiment are very narrow; for example, in a similar experiment in which the mixture was kept at 32° oximination did not take place, and another experiment at 40° yielded mainly the dioximino-derivative.) After addition of water, the mixture was shaken with 10% sodium hydroxide and ether, and the aqueous solution saturated with carbon dioxide and again extracted with ether. The second extract was washed once with sodium hydrogen carbonate solution, dried with sodium sulphate, and evaporated. The residue, after draining on porous porcelain, was washed with ligroin containing a little xylene to remove coloured impurities, and then extracted with hot ligroin, in which the dioximino-compound is only slightly soluble. The solution on cooling deposited colourless needles, m. p. about 105° (Found: N, 8·5. $C_9H_{15}O_2N$ requires N, 8·3%); these probably

contained traces of the dioximino-compound, which, with the small quantities at our disposal, we have been unable to eliminate. In its general reactions, however, this oxime closely resembles the γ-oxime described above: for instance, it gives a pale red-brown colour with ferric chloride, reduces Fehling's solution, and on hydrolysis by means of hydrochloric acid yields the hydroxy-ketone (m. p. 86°). Similar results have been obtained by using nitrosyl chloride in place of *iso*amyl nitrite and sodium methoxide, but here again we have been unsuccessful in establishing the conditions for a satisfactory preparation. On the two occasions in which the mono-oximino-compound was isolated, chloroform was employed as solvent, and in one case the temperature was 0°, and in the other 15°. Upwards of a dozen similar experiments, with ether, ligroin, or chloroform as solvent, and at temperatures ranging from −12° to +15°, yielded the dioximino-compound unaccompanied by any appreciable quantity of the mono-oximino-derivative.

An isomeric oximino-compound was obtained under the following conditions. A solution of the ketone (0·6 g.) in methyl-alcoholic sodium methoxide (0·5 c.c. of a solution prepared from 0·12 g. of sodium and 4 c.c. of methyl alcohol) was kept at 60—65° while *iso*amyl nitrite (0·5 g.) was added very slowly through a capillary tube. The *sodium* salt which separated during this treatment (0·15 g., m. p. 200°) was drained from the adhering mother-liquor, washed with ether and ligroin, and decomposed in aqueous solution by means of carbon dioxide. The *δ-oxime monohydrate* precipitated was crystallised from water and obtained as clusters of colourless needles, m. p. 83° (Found: C, 57·7, 57·9; H, 8·7, 8·9. $C_9H_{17}O_3N$ requires C, 57·8; H, 9·1%). On keeping it in a vacuum at 100° over phosphorus pentoxide, the anhydrous *δ-oxime* is obtained as a white powder, m. p. 170—172°, which, on crystallisation from carbon tetrachloride–ligroin, gives colourless needles, m. p. 172° (Found: N, 8·3. $C_9H_{15}O_2N$ requires N, 8·3%), and on crystallisation from water passes back into the monohydrate, m. p. 83°. This oxime gives a strong red colour with ferric chloride, a blue-green precipitate with cupric acetate, and reduces Fehling's solution. An attempt to hydrolyse the compound by boiling with concentrated hydrochloric acid and formaldehyde led to the production of ααββ-tetramethylglutaric acid (m. p. 144°; mixed m. p., the same). This may be explained on the assumption that a Beckmann change first takes place, producing tetramethylglutarimide, which is then hydrolysed; the explanation would accord with the supposition that the γ- and δ-oximes are stereoisomeric, since the γ-oxime on re-arrangement yields an isomeride of the glutarimide.

Reduction of the Methyl Derivative of the Hydroxy-ketone.—The

reduction product, *5-methoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone*, is obtained as a by-product in the preparation of 5-methoxy-2 : 2 : 3 : 3-tetramethyl-Δ^5-*cyclo*penten-4-one by reduction of its bromo-derivative with zinc dust and boiling glacial acetic acid, and it can be separated from the accompanying unsaturated ketone by fractional distillation. The unsaturated ketone can be reduced to the dihydro-derivative by the same method, but it is difficult to induce the reaction to proceed to completion, and hence fractional distillation is again necessary. The following method gives satisfactory results. The methoxytetramethyl*cyclo*pentanone is treated with 15 times its weight of 2·5% sodium amalgam in boiling glacial acetic acid, and the product is extracted with ether after being poured into water. The extract is washed with sodium carbonate solution and dried and the residue obtained on evaporation is distilled. The saturated methoxy-ketone is a colourless oil, b. p. 88—90°/10 mm., $n_D^{19°}$ 1·4580; b. p. 90°/11 mm.; b. p. 90—92°/13—14 mm., $n_D^{19°}$ 1·4574 (three different preparations) (Found: C, 70·2; H, 10·4; OMe, 18·0. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%. $C_9H_{15}O{\cdot}OMe$ requires OMe, 18·2%). The oxime is an oil which could not be crystallised, and it was not found possible to prepare a solid semicarbazone or phenylhydrazone.

Unlike 5-acetoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone, the saturated methoxy-ketone shows little tendency to undergo further reduction to a tetramethyl*cyclo*pentanone on treatment with zinc or sodium amalgam in acetic acid solution, although we have observed the characteristic camphor-like odour in some experiments.

When the methyl derivative of the hydroxy-ketone is reduced by boiling with concentrated hydriodic acid, *3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone* is formed, which was identified directly and through its semicarbazone. Since methyl iodide is also produced, we assume that demethylation with the formation of the tautomeric hydroxy-ketone constitutes the first stage in the reaction.

*Reduction of 5-Methoxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone Oxime.*—The oxime (p. 390) was reduced with 5 times its weight of sodium in boiling ethyl alcohol, and after acidification with dilute acetic acid and extraction with ether, the free base was liberated by addition of alkali and extracted. The product was similar in all respects to 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine and was identified by the analysis and properties of the picrate and acetyl derivative and by mixed m. p. determinations with authentic specimens.

*Reduction of 5-Methoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone Oxime.*—The oxime (above) prepared from the methoxy-ketone

(1·7 g.), hydroxylamine hydrochloride (1·4 g.), and anhydrous sodium acetate (1·65 g.) by boiling in alcoholic solution for 2 hours, was reduced with sodium (4 g.) in boiling ethyl alcohol. The product, 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine, was isolated and identified as in the preceding experiment.

Action of Hydroxylamine on the p-*Bromobenzyl Derivative of the Hydroxy-ketone.*—The *p*-bromobenzyloxy-compound (0·8 g.), hydroxylamine hydrochloride (0·4 g.), and anhydrous sodium acetate (0·8 g.) were heated for 2 hours in absolute alcohol on the steam-bath. The solid precipitated from the filtered solution by addition of ice-water was collected, dried, dissolved in ether, and treated with hydrogen chloride. The *oxime hydrochloride*, m. p. 133° (decomp.) (Found, by estimation of hydrochloric acid in the aqueous solution: Cl, 9·3. $C_{16}H_{20}O_2NBr,HCl$ requires Cl, 9·5%), which rapidly crystallised, was collected, washed with ether, and dried in a vacuum (yield, 40—50%). The ethereal filtrate, on evaporation, gave a rapidly solidifying oil consisting of the unaltered *p*-bromobenzyloxy-ketone. The hydrochloride was basified with warm aqueous-alcoholic sodium carbonate, and when solution was complete the liquid was diluted with water and cooled to 0°. The *oxime* which separated (m. p. 170—172°) crystallised from dilute alcohol in colourless needles, m. p. 175° (Found: C, 57·3; H, 6·2; N, 4·0, 3·9. $C_{16}H_{20}O_2NBr$ requires C, 56·5; H, 6·2; N, 4·1%). It reduces Fehling's solution.

Reduction of the Oxime and its Acetyl Derivative.—We were unable to obtain satisfactory results on reducing the free oxime either by sodium wire and boiling alcohol or by sodium amalgam in boiling acetic acid. In each case very small amounts of basic material were isolated which gave an impure picrate, m. p. about 202—203°, and the reduction appeared to yield mainly non-basic substances which have not been identified.

The oxime (1·6 g.) was therefore converted into its *acetyl* derivative by treatment with pure acetyl chloride (0·5 c.c.) in dry pyridine solution. The mixture was heated for a short time to complete the reaction, and then poured into water and extracted with ether. The extract was washed successively with water, dilute hydrochloric acid, dilute potassium hydroxide solution, and water, dried and evaporated. The residual oil solidified on being rubbed with ligroin; the product then crystallised from dilute alcohol as thin prisms, m. p. 84° (yield, 1·3 g.) (Found: C, 56·6; H, 6·1. $C_{18}H_{22}O_3NBr$ requires C, 56·8; H, 5·8%). This substance on reduction with sodium and boiling alcohol yielded a considerable amount of a non-basic product, which in the crude state had an odour of toluene, and on draining and crystallising from chloroform

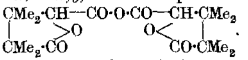
yielded colourless needles, which melted at 161—162° and decomposed a few degrees higher. This substance seemed pure, but on analysis gave figures (C, 69·7, 69·5; H, 5·0, 4·7; N, 6·45, 6·5%) to which we can assign no simple formula. It gives no colour with ferric chloride, is insoluble in water and dilute acids and alkalis, and does not reduce Fehling's solution. Accompanying it in the crude neutral product is an oil which gives a deep crimson colour with ferric chloride. Besides these non-basic substances, an oily base was isolated, which yielded a picrate, m. p. 213° (decomp.) without purification, m. p. 215° (decomp.) after crystallisation from methyl alcohol–ether (Found: C, 46·9, 47·0; H, 5·9, 5·8; N, 14·6, 14·8. $C_{15}H_{22}O_8N_4$ requires C, 46·6; H, 5·7; N, 14·5%). The compound thus appears to be the *picrate* of *2-hydroxy-3:3:4:4-tetramethyl*-cyclo*pentylamine*. A mixture with the isomeric picrate (p. 400) melted at about 195°.

Reduction of the p-*Bromobenzyl Derivative of the Hydroxy-ketone*.—On treatment with sodium amalgam in glacial acetic acid, under conditions in which the corresponding methyl compound is converted into its dihydro-derivative, no reduction occurs, the original substance being recovered unaltered (m. p. 85°. Found: C, 59·1; H, 5·8%). On reduction by means of boiling concentrated hydriodic acid 3:3:4:4-tetramethyl*cyclo*pentanone is formed (identified directly and through the semicarbazone), together with *p*-bromobenzyl iodide. We suppose that dealkylation constitutes the first stage of this reaction.

Examination of the Oily By-product obtained in the Alkylation of the Bromohydroxy-compound with p-*Bromobenzyl Bromide*.—This was reduced under the conditions used for the reduction of the crystalline bromo-*p*-bromobenzyl compound (p. 390), and the product, an oil, was converted into its oxime, also an oil which could not be purified. On reduction by means of sodium and boiling alcohol, this was moderately smoothly converted into 2:2:3:3-tetramethyl*cyclo*pentylamine, which was identified in the manner already described.

Action of Oxidising Agents on the Bromohydroxy-compound.—(1) *Sodium chlorate*. A solution of the bromohydroxy-compound (5 g.), sodium chlorate (13·0 g.), and osmium tetroxide (0·3 g.) in 150 c.c. of water containing a small excess of sodium hydroxide was kept at 40° in a thermostat for 72 hours; a considerable amount of chloride had then been formed. The solution was evaporated to a small bulk, cooled, filtered from the excess of sodium chlorate, acidified, and repeatedly extracted with ether. The residue, which readily solidified, was found to be separable by a prolonged series of fractional crystallisations from chloroform–ligroin into the lactonic

acid of γγ-dihydroxy-ααββ-tetramethylglutaric acid and the lactonic acid of γ-hydroxy-ααββ-tetramethylglutaric acid. A more rapid method of proving the presence of these two substances is the following. The mixed acids were boiled for 1 hour with excess of acetic anhydride and the product was distilled under reduced pressure. After the excess of acetic anhydride had passed over, a small fraction was obtained, b. p. 150—200°/15 mm., and then the main bulk distilled at 220—245°/15 mm. The small fraction solidified, and after crystallisation was identified as the lactonic acid of the γ-hydroxy-γ-acetoxy-ααββ-tetramethylglutaric acid, m. p. 148°, described by Rothstein and Shoppee (*loc. cit.*). The main fraction, which also solidified, crystallised from benzene–ligroin in prisms, m. p. 177—178° (Found: C, 61·0; H, 7·7. $C_{18}H_{26}O_7$ requires C, 61·0; H, 7·4%). The compound is therefore the *dilactone anhydride*,



. On hydrolysis it yields the lactonic acid, m. p. 68°, of γ-hydroxy-ααββ-tetramethylglutaric acid.

(2) *Potassium permanganate.* The bromohydroxy-compound (2·2 g.) was treated with potassium permanganate (1·0 g.) in acetone solution at 0° in the presence of excess of carbon dioxide. After evaporation with water, filtration, and acidification, the acid product was extracted with ether and identified as the lactonic acid of αα-dihydroxy-ααββ-tetramethylglutaric acid (compare Francis and Willson, *loc. cit.*).

(3) *Potassium ferricyanide.* The bromohydroxy-compound (2·0 g.) was kept at 80° for 96 hours in an aqueous solution containing 18 g. of potassium ferricyanide and 4 g. of potassium carbonate. The product extracted with ether after acidification was the same lactonic acid.

(4) *Chromium trioxide.* Experiments were carried out with quantities of chromium trioxide corresponding with 1, 3, and 6 atoms of available oxygen, in glacial acetic acid solution. In each case, tetramethylsuccinic acid was obtained and no earlier product of oxidation could be recognised. The acid was isolated by distillation in steam, during which it probably passed over as its anhydride, which became rehydrated in the receiver. It was extracted from the distillate with ether, and crystallised from chloroform–ligroin containing only a very little alcohol (m. p. 190°).

(5) *Hydrogen peroxide.* The bromohydroxy-compound (2·4 g.) was dissolved in acetone and oxidised at the ordinary temperature with 6 c.c. of 6% aqueous hydrogen peroxide containing a little potassium carbonate. Acidification and extraction with ether

yielded only the lactonic acid of the αα-dihydroxytetramethylglutaric acid.

Action of Oxidising Agents on the Bromomethoxy-compound.—(1) *Ozone.* The methoxy-derivative (4·0 g.) was treated in chloroform solution with a stream of ozonised oxygen for 72 hours. Bromine was evolved, which the excess of oxygen carried over into a trap containing cooled chloroform, in which the bromine dissolved and was identified. The oily ozonides obtained after evaporation of the solvent in a vacuum were decomposed by shaking in ethereal solution (100 c.c.) with acetic acid (10 c.c.) and zinc dust (5 g.). The diluted and filtered solution was extracted with ether, and separated into neutral and acid fractions by means of aqueous sodium carbonate. The neutral portion on distillation yielded a fraction (1·5 g.), b. p. 155—165°/13 mm., which was shown by analysis and hydrolysis to consist essentially of the *lactone* of *methyl hydrogen γγ-dihydroxy-ααββ-tetramethylglutaric acid* (Found: C, 56·3; H, 7·3. $C_{10}H_{16}O_5$ requires C, 55·6; H, 7·5%), although it was probably impure, since we could not crystallise it. A fraction, b. p. 165—210°/13 mm., was also obtained, but its nature was not ascertained. The acid fraction yielded a small quantity of an oil which after some days partly solidified. The crystalline portion was identified by direct comparison and a mixed m. p. determination with the substance (m. p. 103°) described by Rothstein and Shoppee (*loc. cit.*) as dimethyl γ-keto-ααββ-tetramethylglutarate (Found: C, 57·3; H, 8·1. Calc.: C, 57·4; H, 7·9%). It is probably identical with the product, m. p. 93—97°, obtained by Francis and Willson (*loc. cit.*) by the action of diazomethane on the lactonic acid of γγ-dihydroxy-ααββ-tetramethylglutaric acid. Its formation in the reactions now described is very remarkable and suggests the implication of two molecules of the bromomethoxy-compound. Its appearance in the acid fraction may be explained by the supposition that its constitution is really that of the lactone of methyl hydrogen γ-hydroxy-γ-methoxy-ααββ-tetramethylglutarate, which would be soluble in alkali with ring fission, and, assuming its identity with Francis and Willson's methylation product, this structure corresponds with their method of preparation. It is readily soluble in cold 10% potassium hydroxide solution.

(2) *Potassium permanganate.* A solution of the bromomethoxy-compound (1·0 g.) in aqueous acetone containing sodium hydrogen carbonate was oxidised with potassium permanganate (0·38 g., = 1 atom of available oxygen), which was added gradually with stirring. The product, when worked up for organic acids in the usual way, yielded the lactonic acid of the dihydroxytetramethylglutaric acid.

*Ozonolysis of the Bromo-*p*-benzyloxy-compound.*—A solution of this substance (6·0 g.) in glacial acetic acid was treated with ozonised oxygen for several days. Bromine was liberated, and that carried over by the oxygen was caught in cooled chloroform and identified. The ozonides were decomposed by boiling with water, and the products were separated into a neutral and an acid fraction by means of ether and sodium carbonate. The neutral product was a yellow oil which, on treatment with semicarbazide acetate in aqueous alcohol, gave an immediate precipitate of p-*bromobenzaldehyde-semicarbazone,* which separated from alcohol in pearly plates, m. p. 232° (Found: C, 39·4; H, 3·3. $C_8H_8ON_3Br$ requires C, 39·7; H, 3·3%). The aqueous-alcoholic filtrate on dilution with water gave a small precipitate consisting of the unchanged bromo-*p*-benzyloxy-compound. The acid product contained two substances differing in solubility in water. The sparingly soluble compound was identified as *p*-bromobenzoic acid (leaflets from alcohol, m. p. 250°). A small amount of the same substance was collected from the chloroform solution of the ozonides. The soluble acid was obtained as an oil which became largely solid. The drained solid on crystallisation from chloroform–ligroin had m. p. 180—185° (decomp.), and was identified as tetramethylsuccinic acid by direct comparison with a specimen of this substance.

Action of Oxidising Agents on the Bromoacetoxy-compound.—(1) *Ozone.* The bromoacetoxy-compound (3·0 g.) was treated with ozonised oxygen in glacial acetic acid solution until no further absorption of ozone occurred. A yellow colour, which was not due to the liberation of bromine, was produced and disappeared on reduction of the ozonides with zinc dust after addition of ether. In another experiment the bromoacetoxy-compound was treated with ozone in chloroform solution, and here also no liberation of bromine took place. In this case, the ozonides were decomposed by boiling with water. Both experiments yielded tetramethylsuccinic acid (m. p. 190°. Found: C, 55·1; H, 8·4. Calc.: C, 55·1; H, 8·1%), and an acid gum the nature of which was not determined.

(2) *Potassium permanganate.* This experiment was carried out in the same way as the corresponding experiment with the bromomethoxy-compound. It yielded the same lactonic acid, which was obtained by crystallising the crude acid product from ethyl acetate–ligroin.

Oxidation of the Hydroxy-ketone.—Oxidation was effected by excess of 6% hydrogen peroxide in the presence of sodium carbonate at the ordinary temperature. The solution was extracted with ether, acidified, and again extracted. The residue from the second

extraction yielded ααββ-tetramethylglutaric acid, which was crystallised from ethyl acetate–ligroin (leaflets, m. p. 144°. Found: *M*, 190; C, 57·2; H, 8·4. Calc.: *M*, 188; C, 57·4; H, 8·5%).

Oxidation of 2 : 2 : 3 : 3-*Tetramethyl*cyclo*pentanone*.—Oxidation is not easily effected by means of cold neutral potassium permanganate in acetone, although ααββ-tetramethylglutaric acid can be obtained in this way in small yield. More satisfactory results were obtained by boiling the ketone under reflux with nitric acid (*d* 1·20) until oxides of nitrogen ceased to be evolved, the ketone which collected in the condenser being returned to the liquid from time to time. The nitric acid solution was extracted with a large volume of ether, and the extract was washed six times with small amounts of water, dried, and evaporated. The solid residue, after being washed with benzene and crystallised from ethyl acetate–ligroin, was identified as ααββ-tetramethylglutaric acid (m. p. 144°) by direct comparison and mixed m. p. determination. A further small quantity was obtained by evaporation of the aqueous washings.

Bromination of the Hydroxy-ketone.—(1) *In chloroform*. The hydroxy-ketone readily absorbs 2 atoms of bromine in cold chloroform, but an excess over this quantity is not decolorised. On removing the chloroform, hydrogen bromide and excess of bromine, the bromohydroxy-compound is obtained in an almost pure state (m. p. 115—116°; after purification, m. p. 116°).

(2) *In glacial acetic acid*. In this solvent 4 atoms of bromine are rapidly absorbed and the product is the orange dibromo-diketone (m. p. 182°) described by Francis and Willson.

Dichlorophorone (1 : 4-*Dichloro*-2 : 2 : 3 : 3-*tetramethyl*-[0,1,2]-dicyclo*pentanone*).—Phorone tetrachloride (m. p. 59°) and dichlorophorone (b. p. 115—117°/18 mm., $n_D^{24°}$ 1·5074, $d_4^{24°}$ 1·1661; compare Hellthaler, *Annalen*, 1919, **406**, 150) were obtained by methods similar to those used for the preparation of the bromine analogues.

1-*Chloro*-2 : 2 : 3 : 3-*tetramethyl*-[0,1,2]-dicyclo*pentan*-4-*ol*-5-*one* (1-*Chloro*-2 : 2 : 3 : 3-*tetramethyl*-Δ^5-cyclo*penten*-5-*ol*-4-*one*).—This was prepared by hydrolysis of dichlorophorone, following Francis and Willson's method for the corresponding bromine derivatives, and crystallised from dilute alcohol, from which it separated in well-formed, colourless needles, m. p. 116° (Found: C, 57·2; H, 6·9. $C_9H_{13}O_2Cl$ requires C, 57·2; H, 6·9%).

The *acetyl* derivative, prepared in the same way as its bromo-analogue, separates from dilute alcohol in prisms, m. p. 47° (Found: C, 57·3; H, 6·5. $C_{11}H_{15}O_3Cl$ requires C, 57·2; H, 6·5%).

1 : 1-*Dichloro*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione*.—This substance was prepared from the chlorohydroxy-compound by treat-

ment with excess of chlorine in cold glacial acetic acid solution. It separates from alcohol in orange, foliated masses, m. p. 187° (*Found : C, 48·6; H, 5·5.* $C_9H_{12}O_2Cl_2$ *requires C, 48·4; H, 5·4%).*

On boiling in aqueous-alcoholic solution with addition of carbamide to destroy the hypochlorous acid, the chlorohydroxy-compound is formed.

1-*Chloro*-1-*bromo*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione* was prepared by the action of bromine in acetic acid solution on the chlorohydroxy-compound, and crystallised from alcohol in orange, foliated masses, m. p. 178° (Found : C, 40·9; H, 4·8. $C_9H_{12}O_2ClBr$ requires C, 40·4; H, 4·5%). The same substance is formed when the bromohydroxy-compound is treated with chlorine in acetic acid, but in this case an unidentified colourless by-product, m. p. 197°, is also formed in small amount.

Reduction with boiling aqueous-alcoholic carbamide yields the chlorohydroxy-compound exclusively. Since the bromo- and chlorohydroxy-compounds melt at the same temperature and give somewhat small m. p. depressions in admixture, the reduction product was converted into its acetyl derivative (bromo-, m. p. 74°; chloro-, m. p. 47°) which was crystallised in fractions from dilute alcohol, in which the bromoacetoxy-compound is less soluble than its chloro-analogue; all the fractions had m. p. 47°.

1 : 1-*Dibromo*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanedione*.—This substance (herring-bone-like clusters of orange rhomboids, m. p. 182°. Found : C, 34·6; H, 3·9. Calc. : C, 34·7; H, 3·8%), which Francis and Willson found to be reduced incompletely by boiling with water or alcohol, is, like its analogues, quantitatively converted into the halogenohydroxy-compound by boiling with aqueous-alcoholic carbamide.

This paper is published mainly in order to place on record the observations which have accumulated during the four years in which the work has been in progress; but it is realised that, in constitutional problems of this character, conclusions must necessarily be regarded as provisional, and accordingly further experiments on α-ketols and dialkylideneketones are in progress, which may help to resolve some of the issues raised. We would mention that the method of correlating the tautomeric substances, through their oximes or derivatives of their oximes, with the saturated cyclic amines, which has yielded illuminating results, was originally suggested to us by Mr. W. A. Wightman, and that on many occasions Dr. F. R. Goss has placed his time and great skill in micro-analytical technique at our service. Generous assistance in defraying the heavy cost of the investigation has been given by the Royal Society

and the Commissioners of the 1851 Exhibition, to whom our thanks are due. At one stage the continuity of the work was maintained by means of a valuable gift of the bromohydroxy-compound from Professor Francis.

THE UNIVERSITY, LEEDS. [*Received, December 17th*, 1927.]

LV.—*The Parachor and Chemical Constitution. Part VIII. Ring-chain Valency Tautomerism in Phorone Derivatives.*

By SAMUEL SUGDEN.

DURING the course of the investigation described in the preceding paper, Professor Ingold and Dr. Shoppee were good enough to allow the author to determine the parachor of a number of the substances which exhibit this peculiar type of tautomeric change. The present paper records the data obtained for the surface tension and density of these substances together with a brief discussion of the effect of the changes in structure upon the parachor.

The large amount of chemical evidence accumulated by Ingold and Shoppee indicates that substitution in the $\alpha\alpha'$-positions in phorone produces, to a greater or less degree, a change in structure from the open-chain configuration (I) to the dicyclic structure (II)

$$\text{(I.)}\quad O{=}C\begin{matrix}\diagup CX{=}CMe_2\\ \diagdown CX{=}CMe_2\end{matrix} \quad\rightleftarrows\quad O{=}C\begin{matrix}\diagup CX{-}CMe_2\\ \quad |\qquad |\\ \diagdown CX{-}CMe_2\end{matrix}\quad\text{(II.)}$$

This should bring about a considerable diminution in the parachor since two non-polar double bonds with a parachor of $2 \times 23{\cdot}2$, are replaced by ring structures which have smaller parachors. The constants for the rings concerned have been determined by Sugden and Wilkins (J., 1927, 139) and have the values : 3-ring 16·7, 4-ring 11·6, 5-ring 8·5.

The parachors found for the phorone derivatives are collected in Table I in the column headed "$[P]$ obs." The next column gives the parachor calculated on the assumption that the substance is a derivative of phorone and contains two double bonds. It will be seen that, whereas phorone has a nearly normal parachor, the di-bromo-derivative has a large negative anomaly which becomes still larger in the oxy- and bromo-oxy-derivatives. The general trend of the parachors is therefore in good agreement with the conclusions as to structure reached by Ingold and Shoppee, since the dibromo compound exhibits the reactions of both open-chain and cyclic structures, and the oxy- and bromo-oxy-derivatives behave chemically as if they consisted entirely of the isomeride of formula (II).

TABLE I.

Substance.	[P] obs.	[P] calc.	Anomaly.
Phorone	367·9	372·2	− 4·3
Dichlorophorone	427·7	446·6	−18·9
Dibromophorone	463·2	474·0	−10·8
Acetoxyphorone	459·4	476·0	−16·6
Bromoacetoxyphorone	506·4	526·9	−20·5
Bromomethoxyphorone	455·3	482·1	−26·8
Benzoyloxyphorone	583·9	609·9	−26·0
Bromobenzoyloxyphorone	642·4	660·8	−18·4
p-Bromobenzyloxyphorone	630·7	655·0	−24·3
Bromo-*p*-bromobenzyloxyphorone	684·0	705·9	−21·9
Distyryl ketone	564·5	562·0	+ 2·5
Dibromodistyryl ketone	650·7	663·8	−13·1

The largest anomaly found occurs with bromomethoxyphorone (−26·8), and nearly the same value is reached by benzoyloxy- and *p*-bromobenzyloxy-phorone. The last two substances were crystallised to constant melting point, and hence there is little doubt as to their purity. Three specimens of the bromomethoxy-derivative, prepared by different methods, were examined, and all had the same surface tensions and densities; hence it is very improbable that this liquid product contained any appreciable amount of impurity. The mean anomaly for these three substances (−25·7) may therefore be taken to represent the effect of complete conversion into the bicyclic form, from which it follows that the structural constant for the fused-ring structure in (II) has the value 46·4 −25·7 = 20·7.

There is at present little information as to the relation between the constant for fused-ring structures and those for the isolated rings of which they may be supposed to be composed. The *cyclo*propene esters examined by Sugden and Wilkins (*loc. cit.*) gave a constant approximately equal to the sum of the double-bond and 3-ring constants, whilst benzene and many of its derivatives give parachors which can be predicted accurately by using a structural constant equal to the 6-ring constant + three double bonds. It seems probable, therefore, that the fused-ring structure in (II) may be regarded as composed of a five-membered ring upon which is superimposed the effect of a three-membered ring giving a constant of 16·7 + 8·5 = 25·2. This is nearly 5 units higher than the value found for the fully cyclised phorone derivatives, but the difference is probably due to the effect of the two *gem*-dimethyl groups which are known to stabilise ring structures and diminish unsaturation. In the series of *cyclo*propane esters studied by Sugden and Wilkins (*loc. cit.*), the presence of *gem*-carbethoxyl groups produced a marked lowering of the constant for a three-membered ring which, with two such groupings in the molecule, fell to 12·9. In this connexion,

it is worthy of note that phorone shows a small negative anomaly although there is no chemical evidence for the presence of the cyclic isomeride, whilst distyryl ketone, in which the *gem*-dimethyl groups are replaced by phenyl, has a parachor slightly higher than the calculated value. The dibromo-derivative of this ketone shows, however, a marked negative anomaly, indicating partial conversion to the bicyclic form.

Acetoxyphorone is found by Ingold and Shoppee to behave as if it were a *cyclo*pentene derivative; this would correspond to an anomaly of $-14{\cdot}7$ which is in good agreement with the value found, *viz.*, $-16{\cdot}6$, when allowance is made for the effect of the *gem*-dimethyl groups.

In general, therefore, the parachors of these substances exhibit changes which confirm the structural conclusions reached by Ingold and Shoppee. Incidentally it may be noted that they supply a further example of the relation between parachor constants and unsaturation which has been discussed in earlier papers of this series.

It is noteworthy that the parachors of substances such as dibromophorone which are presumably equilibrium mixtures of isomerides show no appreciable change with temperature. The composition of the equilibrium mixture must therefore remain nearly constant, from which it follows that the heat evolved or absorbed by the change from the open chain to the bicyclic structure must be small. If this is correct the isomerides are substances which differ in reactivity (unsaturation) but have nearly the same energy content.

EXPERIMENTAL.

The determination of the parachor involves the measurement of the surface tension and density at a series of temperatures; the parachor is then calculated by the formula $[P] = M\gamma^{\frac{1}{4}}/(D - d)$, where M is the molecular weight, γ the surface tension in dynes/cm., and D and d the density of the liquid and vapour respectively in g./c.c. For the substances described below, d is very small at the temperature of observation and has been neglected.

Densities were determined with a U-shaped pyknometer, and surface tensions by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). To save space the observed pressures are not recorded but only the surface tensions deduced therefrom.

Phorone, $C_9H_{14}O$, $M = 138{\cdot}2$, m. p. 28°. Densities determined: $D_{4^\circ}^{30^\circ} = 0{\cdot}880$, $D_{4^\circ}^{50^\circ} = 0{\cdot}864$, $D_{4^\circ}^{69^\circ} = 0{\cdot}848$, $D_{4^\circ}^{89^\circ} = 0{\cdot}830$, whence $D_{4^\circ}^{t^\circ} = 0{\cdot}906 - 0{\cdot}00084t$.

t	29·5°	51·5°	71°	99°	
γ	30·22	27·94	25·77	22·88	
D	0·881	0·863	0·846	0·823	
Parachor	367·8	368·3	368·2	367·3	Mean = 367·9

αα′-Dichlorophorone, $C_9H_{12}OCl_2$, $M = 207{\cdot}1$, b. p. 119—121°/17 mm. Densities determined: $D_{4°}^{19°} = 1{\cdot}173$, $D_{4°}^{57°} = 1{\cdot}136$, $D_{4°}^{88°} = 1{\cdot}107$, whence $D_{4°}^{t°} = 1{\cdot}191 - 0{\cdot}00095t$.

t	21°	41°	59°	83°	
γ	33·97	32·31	30·15	27·79	
D	1·171	1·152	1·135	1·112	
Parachor	427·0	428·7	427·6	427·3	Mean = 427·7

αα′-Dibromophorone, $C_9H_{12}OBr_2$, $M = 296{\cdot}0$, m. p. 32°. Densities determined: $D_{4°}^{33°} = 1{\cdot}556$, $D_{4°}^{50{\cdot}5°} = 1{\cdot}534$, $D_{4°}^{73{\cdot}5°} = 1{\cdot}505$, whence $D_{4°}^{t°} = 1{\cdot}598 - 0{\cdot}00126t$.

t	31·5°	49·5°	67·5°	
γ	35·31	33·38	31·46	
D	1·558	1·536	1·513	
Parachor	463·2	463·1	463·2	Mean = 463·2

α-Acetoxyphorone, $C_{11}H_{16}O_3$, $M = 196{\cdot}2$, b. p. 109°/3 mm. Densities determined: $D_{4°}^{16°} = 1{\cdot}024$, $D_{4°}^{38°} = 1{\cdot}004$, $D_{4°}^{58{\cdot}5°} = 0{\cdot}986$, $D_{4°}^{78°} = 0{\cdot}969$, whence $D_{4°}^{t°} = 1{\cdot}038 - 0{\cdot}00088t$.

t	16·5°	43·5°	61·5°	84°	
γ	32·64	30·12	28·29	26·08	
D	1·023	1·000	0·984	0·964	
Parachor	458·3	459·6	459·8	459·9	Mean = 459·4

α-Bromo-α′-acetoxyphorone, $C_{11}H_{15}O_3Br$, $M = 275{\cdot}1$, m. p. 74°. Densities determined: $D_{4°}^{89°} = 1{\cdot}256$, $D_{4°}^{110°} = 1{\cdot}234$, $D_{4°}^{133{\cdot}5°} = 1{\cdot}210$, whence $D_{4°}^{t°} = 1{\cdot}348 - 0{\cdot}00103t$.

t	80°	101°	120°	142·5°	
γ	29·45	27·53	25·84	23·80	
D	1·266	1·244	1·244	1·201	
Parachor	506·2	506·6	506·7	506·0	Mean = 506·4

α-Bromo-α′-methoxyphorone, $C_{10}H_{15}BrO_2$, $M = 247{\cdot}1$, b. p. 133° 25 mm. Densities determined: $D_{4°}^{23{\cdot}5°} = 1{\cdot}314$, $D_{4°}^{42°} = 1{\cdot}294$ $D_{4°}^{60{\cdot}5°} = 1{\cdot}274$, $D_{4°}^{80{\cdot}5°} = 1{\cdot}253$, whence $D_{4°}^{t°} = 1{\cdot}339 - 0{\cdot}00107t$.

t	17·5°	46°	67·5°	89°	
γ	34·86	32·02	29·87	27·73	
D	1·320	1·290	1·267	1·244	
Parachor	454·8	455·6	455·9	455·8	Mean = 455·5

Another specimen prepared from the silver salt and measured with a different pyknometer and bubbler gave the following results $D_{4°}^{12°} = 1{\cdot}327$, $D_{4°}^{40{\cdot}5°} = 1{\cdot}298$, $D_{4°}^{55°} = 1{\cdot}282$, $D_{4°}^{73{\cdot}5°} = 1{\cdot}263$, whence $D_{4°}^{t°} = 1{\cdot}339 - 0{\cdot}00104t$.

t	13°	38°	67°	
γ	35·45	32·86	29·81	
D	1·326	1·299	1·269	
Parachor	454·8	455·4	455·0	Mean = 455·1

P

A third specimen gave the following values for the paracho 11·5°, 454·3; 32°, 455·3; 48°, 454·7; 61·5°, 455·9; 74·5°, 455·8 mean 455·2. It is very improbable, therefore, that this substanc contains an appreciable amount of impurities, since modification in the method of preparation and isolation gave a product wit] constant physical properties.

α-Bromo-α′-benzoyloxyphorone, $C_{16}H_{17}O_3Br$, $M = 337·2$, m. p 92°. Densities determined: $D_{4°}^{94°} = 1·264$, $D_{4°}^{116°} = 1·248$, $D_{4°}^{130·5°} = 1·231$, $D_{4°}^{149°} = 1·216$, whence $D_{4°}^{t°} = 1·344 - 0·00086t$.

t	95·5°	117°	136°	162°	
γ	33·22	31·23	29·66	27·35	
D	1·261	1·241	1·224	1·201	
Parachor	642·0	642·6	642·8	642·1	Mean = 642·4

*α-Bromo-α′-*p*-bromobenzyloxyphorone*, $C_{16}H_{18}O_2Br_2$, $M = 402·1$ m. p. 63—64°. Densities determined: $D_{4°}^{73°} = 1·437$, $D_{4°}^{93·5°} = 1·418$, $D_{4°}^{113°} = 1·397$, $D_{4°}^{135·5°} = 1·377$, whence $D_{4°}^{t°} = 1·51($ $- 0·00099t$.

t	73·5°	91°	110°	131°	
γ	35·57	33·93	32·69	30·63	
D	1·437	1·420	1·401	1·380	
Parachor	683·4	683·3	684·1	685·3	Mean = 684·0

α-Benzoyloxyphorone, $C_{16}H_{18}O_3$, $M = 258·2$, m. p. 68°. Densitie; determined: $D_{4°}^{75·5°} = 1·056$, $D_{4°}^{92°} = 1·043$, $D_{4°}^{112·5°} = 1·026$, $D_{4°}^{133·5}$ $= 1·010$, whence $D_{4°}^{t°} = 1·117 - 0·00080t$.

t	75°	93°	117°	131·5°	
γ	32·42	30·82	28·81	27·76	
D	1·057	1·043	1·023	1·012	
Parachor	582·9	582·9	584·4	585·5	Mean = 583·9

*α-*p*-Bromobenzyloxyphorone*, $C_{16}H_{19}O_2Br$, $M = 323·2$, m. p 86—87°. Densities determined: $D_{4°}^{94·5°} = 1·220$, $D_{4°}^{117·5°} = 1·119$ $D_{4°}^{133·5°} = 1·186$, $D_{4°}^{157°} = 1·168$, whence $D_{4°}^{t°} = 1·302 - 0·00087t$.

t	96°	101°	115°	128·5°	146°	154·5°
γ	31·86	31·26	29·99	29·18	27·86	27·14
D	1·218	1·214	1·202	1·190	1·175	1·168
Parachor	630·6	629·5	629·2	631·4	631·8	631·6
			Mean = 630·7			

Distyrylketone, $(CHPh{:}CH)_2CO,C_{17}H_{14}O$, $M = 234·2$, m. p. 112°. Densities determined: $D_{4°}^{116°} = 1·033$, $D_{4°}^{140°} = 1·017$, $D_{4°}^{171°} = 0·995$, whence $D_{4°}^{t°} = 1·118 - 0·00072t$.

t	120°	130°	144·5°	164°	
γ	38·20	37·14	35·72	33·78	
D	1·032	1·024	1·014	1·000	
Parachor	564·2	564·8	564·6	564·6	Mean = 564·5

αα′-Dibromodistyrylketone, $C_{17}H_{12}OBr_2$, $M = 392{\cdot}1$, m. p. 98°. is substance decomposed rapidly a few degrees above its m. p. t showed no appreciable change after 1 hour at 100°. Found : ɩt 100° = 40·07, $D_{4°}^{100°} = 1{\cdot}516$, whence the parachor = 650·7.

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VI.—*The Union of Benzoylacetonitrile with Organic Bases in the Presence of Salicylaldehyde. Part II.*

By PANCHAPAKESA KRISHNAMURTI.

RRESPONDING to the compound formed when benzoylacetonitrile ɩcts with piperidine in the presence of salicylaldehyde as catalyst , 1927, 1349), compounds have now been obtained from aniline, ;oluidine, and *m*-4-xylidine. In all these cases, the addition piperidine in small amounts almost doubled the yields, in ɔordance with the view that the first stage of this type of reaction the formation of a salicylidene derivative under the influence of e base (Krishnamurti and Dey, *loc. cit.*).

›- and *m*-Toluidines did not react with benzoylacetonitrile under › conditions mentioned above. A similar behaviour has been ticed in the addition of bases to nitrostyrene (Worrall, *J. Amer. em. Soc.*, 1927, 49, 1598) : Aniline and *p*-toluidine reacted in the rmal way to give the derivatives, whereas *o*- and *m*-toluidines led to react, and the author came to the conclusion that a sub- ;uent in the ortho- and even in the meta-position to the amino- ›up hinders the mobility of its hydrogen atoms. If this is so, the ctivity of *m*-4-xylidine towards benzoylacetonitrile can only be plained by assuming that the steric effects of one substituent are dified by the presence of other groups in more favourable sitions.

In most respects, the compounds of benzoylacetonitrile with line and with *p*-toluidine were similar to that with piperidine, t they differed from it in that (*a*) they easily gave dibenzoyl ivatives and (*b*) the *iso*nitroso-compounds did not yield acyl ivatives, benzoylation in the usual way producing the benzoyl ivatives of the primary amines.

EXPERIMENTAL.

The p-*Toluidine Compound.*—A solution of benzoylacetonitrile mol.) and *p*-toluidine (1 mol.) in absolute alcohol containing

salicylaldehyde (2—3 drops) and piperidine (1—2 drops) was heated on the water-bath for 8 hours, alcohol being added from time to time to replace that lost by evaporation. The reddish-brown solution was then diluted with much water and acidified with hydrochloric acid, and after 12 hours the clear solution was decanted and treated with an excess of alkali. The *compound* thus precipitated crystallised from alcohol in pale yellow, rhombic prisms (yield, about 50%), m. p. 182° (Found: C, 76·3; H, 6·4; N, 11·3. $C_{16}H_{16}ON_2$ requires C, 76·2; H, 6·35; N, 11·1%).

The *hydrochloride* crystallised from hot dilute hydrochloric acid in colourless needles, m. p. 194—195° (Found: Cl, 12·2. $C_{16}H_{16}ON_2,HCl$ requires Cl, 12·3%). The *dibenzoyl* derivative formed pale yellow, glistening needles, m. p. 166°, from alcohol (Found: C, 78·0; H, 5·1; N, 6·0. $C_{30}H_{24}O_3N_2$ requires C, 78·3; H, 5·2; N, 6·1%).

The iso*nitroso-derivative.* A solution of the base in hot dilute hydrochloric acid was cooled rapidly and a dilute solution of the requisite quantity of sodium nitrite was added, followed after a few minutes by an excess of dilute sodium hydroxide solution. After filtration, the light brown solution was acidified with dilute acetic acid; the iso*nitroso*-derivative thus precipitated crystallised from alcohol in bright orange plates, m. p. 158°, to a reddish-brown liquid (Found: C, 68·5; H, 5·4; N, 15·1. $C_{16}H_{15}O_2N_3$ requires C, 68·3; H, 5·3; N, 14·95%).

Its *silver* salt was obtained as a light pink, curdy precipitate (Found: Ag, 28·0. $C_{16}H_{14}O_2N_3Ag$ requires Ag, 27·8%).

The Aniline Compound.—The conditions of experiment were practically the same as those described for preparing the *p*-toluidine compound. The yield was somewhat lower (about 40%). The substance crystallised from alcohol in light yellow prisms, m. p. 163° (Found: N, 11·7. $C_{15}H_{14}ON_2$ requires N, 11·8%).

The *hydrochloride* crystallised from dilute hydrochloric acid in glistening plates, m. p. 94—96°. The *dibenzoyl* derivative was obtained from alcohol in pale yellow needles, m. p. 168° (Found: N, 6·2. $C_{29}H_{22}O_3N_2$ requires N, 6·3%). The iso*nitroso*-derivative crystallised from alcohol in blood-red plates, m. p. 182° (decomp.) (Found: N, 15·75. $C_{15}H_{13}O_2N_3$ requires N, 15·7%).

The *m-4-xylidine compound* was obtained under the same conditions as the *p*-toluidine compound, the heating, however, being continued for 16 hours (yield, about 20%). It crystallised from benzene in colourless plates, m. p. 145—146° (Found: N, 10·5. $C_{17}H_{18}ON_2$ requires N, 10·5%). Its *benzoyl* derivative crystallised from alcohol in colourless, shining needles, m. p. 153°, and the iso*nitroso*-derivative in yellow plates, m. p. 150—151° to a scarlet liquid.

In conclusion, I wish to thank Professor C. V. Raman, F.R.S., for kindly permitting me to carry out this investigation in his laboratory.

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LVII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXIII. Anomalous Orientation by Halogens, and its Bearing on the Problem of the Ortho–Para Ratio, in Aromatic Substitution.*

By Christopher Kelk Ingold and Charles Cyril Norrey Vass.

The theory that the *op*-directive efficiencies of the halogens in the halogenobenzenes varies directly with the tendency of the halogen atom to share additional electrons $(+T)$ and inversely as its attraction for electrons, shared and unshared $(-I)$, and therefore $(+T-I)$ corresponds to the sequence I>Br>Cl>F, is in accord with much indirect evidence. For example, the relative speeds of nitration of halogenobenzenes indicate I>Br>Cl>F (Ingold and Shaw, J., 1927, 2918), the relative basicities of combined halogens demand I>Br, the data on molecular dipole moments suggest I>Br>Cl, and the substitution of ω-halogenated toluenes requires Cl>F, for the phenomenon under discussion. The same sequence is also in agreement with the available data on the nitration of *o*- and *p*-dihalogenobenzenes with the following significant * exception. Holleman (*Rec. trav. chim.*, 1915, **34**, 216) found that whereas the nitration of *p*-chlorobromobenzene proceeded normally,

Direction by Cl : *Direction by Br* = 45·2% : 54·8% . . (para)

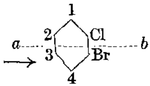
the nitration of *o*-chlorobromobenzene gave an abnormal result :

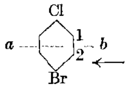
Direction by Cl : *Direction by Br* = 55·5% : 45·5% . (ortho)

The present paper is the result of an attempt to test a possible explanation of this anomaly on the following lines. The inductive effect $(-I)$, which, according to the sequence, should be greater for Cl than for Br, is regarded as originating in a contracted electron shell around the halogen atom, as compared with a hypothetical

* The apparent exception represented by van Hove's recent experiments (*Bull. Acad. roy. Belg.*, 1926, **12**, 801) is not regarded as significant for our purpose in view of the special experimental conditions employed. The point will be dealt with more fully in a future paper.

non-orienting atom having the same number of electrons of each class. This should not only produce electron displacements relayed from bond to bond, but might also, by direct action through space, modify existing electrical fields in such a way that the potentially active electrons of the benzene ring would be subjected to an additioual electrostatic restraint. The " direct " effect of halogens is therefore a deactivating influence ($-D$). Since its genesis is also that of the inductive effect ($-I$), its variation as between different directing atoms will be the same as that of the inductive effect. Because, however, it is propagated, not through the bonds, but through space, its distribution in the ring will be, not in the order $op > m$, but in the order $o > m > p$. The full expression for the directive action of halogens in halogenobenzenes is therefore $+T - I - D$. The modes of distribution in the ring of T and of I were dealt with by Ingold and Shaw (*loc. cit.*).

(A) 

 (B)

Let X and X' represent the intensities of the direct effects due to Cl and Br respectively, so that $X > X'$; and let f, f' and f'' be factors (assumed to be substantially the same for Cl and Br) expressing the distribution of the effect as between the o-, *m*-, and *p*-positions respectively, so that $f > f' > f''$. In o-chlorobromobenzene the direct effects ($-D$) at positions 1, 2, 3, and 4 (A) will be as follows:

$$(1) = fX + f'X', \qquad (2) = f'X + f''X',$$
$$(3) = f''X + f'X', \qquad (4) = f'X + fX'.$$

From the inequalities mentioned it follows, first, that $(1) + (4) > (2) + (3)$ because every term in $fX + f'X + fX' + f'X'$ is greater than the corresponding term in $f'X + f''X + f'X' + f''X'$. That is, in so far as the direct effect controls the situation, substitution will occur mainly at (2) and (3). Secondly since $(2) - (3) = (f' - f'')(X - X') =$ positive, therefore $(2) > (3)$ Hence the direct effect will deactivate position (2) more strongly and will favour substitution at position (3). Similarly, $(1) > (4)$ so that if the molecule be divided symmetrically between the halogens by a line *ab*, the half containing Cl will be deactivated relatively to the half containing Br. In *p*-chlorobromobenzene (B we have

$$(1) = fX + f'X' \qquad \text{and} \qquad (2) = f'X + fX',$$

so that $(1) > (2)$, and here again the rule relating to symmetrica division applies. That is to say, in the para-compound the direc

effect will collaborate with the tautomeric and inductive effects in favouring substitution in position (2), and an anomalous result is not to be expected; but in the ortho-compound the direct effect opposes the other influences, and this might explain the apparent reversal of directive efficiencies observed by Holleman. It is also obvious that the above considerations accord with the small amounts of vicinal substitution observed (Reiding, *Rec. trav. chim.*, 1904, **23**, 359; Holleman, Reiding, Sirks, and Sluiter, *ibid.*, 1906, **25**, 183; 1907, **26**, 153) in the nitration of *o*-dichloro- and *o*-dibromobenzene (see also Holmes, Ingold, Ingold, and Smith, J., 1926, 1684, 3093; 1927, 1690):

and that they afford a partial explanation of such facts as the diminishing *o*-nitration towards fluorobenzene in the series of halogenobenzenes:

	PhF.	PhCl.	PhBr.	PhI.
Ortho	12·7	30·1	37·6	41·1
Para	87·4	69·9	62·1	58·7

(Holleman, Holleman, and de Bruyn, *Rec. trav. chim.*, 1900, **19**, 189, 364; 1903, **22**, 263; 1905, **24**, 140; 1913, **32**, 134), and the displacement from *o*-substitution in the direction of *p*-substitution which occurs on increasing the acidity of the medium employed in the nitration of acetanilide (direct effect of weak dipole arising from loose salt-formation). Again the conception of an influence " distributed over the molecule " by which Allan, Oxford, Robinson, and Smith (J., 1926, 406) explained the diminishing disparity in the directive powers of the groups in an ascending series of the higher alkyl ethers of guaiacol may be translated into the following: The sign of the inductive effect of alkyl groups (+ *I*), established by Lucas and his collaborators (*J. Amer. Chem. Soc.*, 1924, **46**, 2475; 1925, **47**, 1459, 1462) and subsequently confirmed by many orientation experiments, suggests that electrons in the neighbourhood of an alkyl group would suffer repulsion (diminished attraction) by electrostatic action through space; in the high alkyl ethers of guaiacol the field at the two oxygen atoms * due to the direct effect

* Since in orientation by ·OR the tautomeric effect overwhelmingly predominates, it is unnecessary to consider the direct effects at the distant points of reaction in the benzene ring. Furthermore, there is no necessity for the supposition that the effect considered is distributed *equally* between the two oxygen atoms, or between the nuclear positions they respectively activate.

of the larger alkyl group will increase the displacements of the unshared electrons of both oxygen atoms towards the benzene ring. The effects observed are precisely those to be expected, and an intelligible * mechanism is thus provided.

Definite prediction in regard to the direct effect is possible in simple cases, (*a*) because this effect, representing a permanent molecular condition, will follow the inductive, and not the tautomeric, effect in sign and magnitude, so far as concerns its origination (compare Ingold and Shaw, *loc. cit.*); and (*b*) because, once originated, its distribution is a matter of molecular geometry. When considering cases in which the operation of the direct effect might be expected to give rise to notable anomalies, we selected a fluorine compound, because the inductive effect, and therefore presumably the direct effect, is strongest at the fluorine end of the halogen series. Furthermore, the very large disparity in the orientation by fluorine and chlorine observed by Swartz (*Rec. trav. chim.*, 1915, **34**, 131) in the nitration of *p*-fluorochlorobenzene,

Direction by F : *Direction by Cl* = 27·7% : 72·3% . . (para)

(we have confirmed this result) † gave rise to the suspicion that the normal difference between the directive powers of these elements (*i.e.*, that due to $+T-I$) is greatly augmented in this substance by the direct effect ($-D$) in accordance with the theory outlined above. It followed that the small anomaly observed by Holleman in *o*-chlorobromobenzene should become notably increased in *o*-fluorochlorobenzene. We have therefore examined the nitration of the latter and are able to show that the substitution occurs mainly in the two para-positions, as was expected, and that the relative direction by the two halogens is as follows:

Direction by F : *Direction by Cl* = 78·7% : 21·3% . (ortho)

We venture to suggest that this strikingly anomalous result definitely requires a theoretical explanation along the lines indicated; and it is consistent therewith that in the nitration of *o*-bromoiodobenzene ($-D$, much weaker) the anomaly disappears (Holleman, *Rec. trav. chim.*, 1915, **34**, 228).

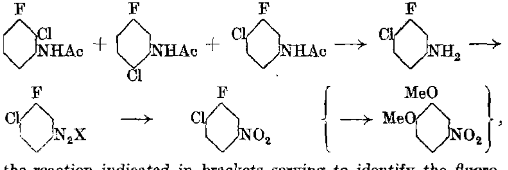
Experimental.

3-Fluoro-4-chloronitrobenzene.—The scheme of preparation was as follows: *m*-Nitroaniline ⟶ *m*-nitrobenzenediazonium fluoride

* We do not mean that it is possible precisely to specify all the details of the mechanism in this or any of the other cases discussed in this paper.

† There is an arithmetical error in Swartz's paper; the figures here shown represent a correct interpretation of his data.

→ *m*-nitrofluorobenzene → *m*-fluoroaniline → *m*-fluoroacetanilide → *N*-chloro-*m*-fluoroacetanilide $\xrightarrow[\text{(re-arrangement)}]{}$



the reaction indicated in brackets serving to identify the fluorochloroacetanilide selected from the mixture obtained by re-arrangement. The process is obviously diagnostic.

Beekman has prepared *m*-fluoronitrobenzene in a somewhat complicated apparatus (*Rec. trav. chim.*, 1904, **23**, 235), and we have obtained an equivalent result by the following simple method. *m*-Nitroaniline (69 g.), suspended in a solution of sulphuric acid (60 g., *d* 1·80) in water (150 g.), was diazotised at 0° with a solution of sodium nitrite (36 g.) in water (50 g.), efficient mechanical stirring being maintained. The product, mixed with 60% hydrofluoric acid (400 c.c.), was distilled from a copper can (2·5 l.) through a copper condenser, and the *m*-nitrofluorobenzene, the last traces of which were driven over with a current of steam, was collected in a rubber beaker, separated from the bulk of the acid liquid by decantation, extracted with ether after addition of alkali, and distilled (b. p. 199—200°; yield 30%). The *m*-fluoroaniline (Wallach and Heusler, *Annalen*, 1888, **243**, 225; Swartz, *Rec. trav. chim.*, 1915, **34**, 131) had b. p. 187—189° (yield 90%), and the *m*-fluoroacetanilide (Swartz, *loc. cit.*) had m. p. 83°, and crystallised usually in rhombs, but occasionally in oblique-ended needles.

m-Fluoroacetanilide (10 g.), suspended in a solution of potassium hydrogen carbonate (30 g.) in water (200 c.c.), was mechanically stirred and treated during 1 hour at the ordinary temperature with an aqueous paste of bleaching powder (32 g.; available Cl, 28%). The stirring was continued for 24 hours, the solution was then acidified with hydrochloric acid, and stirred for a further 12 hours. The mixed fluorochloro-compounds were obtained in approximately theoretical yield by collecting and drying tho precipitate, and extracting the filtrate with ether. The separation of the products necessitated a lengthy series of fractional crystallisations from ethyl acetate-ligroin, and even then was incomplete. Thus from 18 g. of *m*-fluoroacetanilide we obtained the quantities given as yields below, together with much unresolved mixture. 3-*Fluoro-4-chloro-*

acetanilide (yield 9·5 g.) was obtained as glistening plates, m. p. 115° (Found: Cl, 19·3. C_8H_7ONClF requires Cl, 18·9%). Its constitution follows from its conversion into 4-nitroveratrole by the reactions described below. 3-*Fluoro*-6-*chloroacetanilide*, or, less probably, 3-fluoro-2-chloroacetanilide (yield 0·2 g.), was isolated as long, slender needles, m. p. 143° (Found: C, 51·8; H, 4·2. C_8H_7ONClF requires C, 51·2; H, 3·7%). 3-*Fluoro*-4 : 6-*dichloroacetanilide*, or, less probably, 3-fluoro-2 : 6-dichloroacetanilide (yield 0·8 g.), forms prisms, m. p. 124° (Found: C, 43·6; H, 2·9. $C_8H_6ONCl_2F$ requires C, 43·2; H, 2·7%).

3-*Fluoro*-4-*chloroaniline* was obtained by hydrolysing its acetyl derivative with alcohol and sulphuric acid (Perkin's method), but by-products were also formed. The anilide was therefore boiled for 24 hours with 20% hydrochloric acid, and the amine distilled in steam after basification. Isolated by extraction with ether, it had b. p. about 226°, and separated from ligroin in long, fibrous needles, m. p. 61—62° (Found: Cl, 23·8. C_6H_5NClF requires Cl, 24·3%).

For the preparation of 3-*fluoro*-4-*chloronitrobenzene*, the base (6·0 g.) was suspended in water (100 c.c.), containing sulphuric acid (3·84 g., *d* 1·80), and diazotised at − 5° with a solution of sodium nitrite (4·0 g.) in water (100 c.c.). The bright yellow, sparingly soluble diazo-compound so formed was collected and suspended in water (1 l.), and the suspension poured, with vigorous stirring, into a freshly prepared aqueous solution (100 c.c.) of sodium nitrite (40 g.) and cuprocupric sulphite (Chevreul's salt) (15 g.). A rapid evolution of nitrogen occurred, and, 15 minutes later, when a brown deposit had covered the surface of the dark green liquid, the stirring was discontinued, and the faintly acid solution distilled in steam. The oil was extracted with ether from the distillate, and the extract washed with very dilute alkali, dried with calcium chloride, and distilled. The residue (4·0 g.), which was brown and semi-solid at the ordinary temperature, was distilled and the nitro-compound was then obtained (2·7 g.) as a pale yellow oil, b. p. 114—116°/24 mm., which crystallised in the receiver. It was finally purified by crystallisation from ligroin and obtained as very pale yellow leaflets, m. p. 63—64° (Found: Cl, 20·7. $C_6H_3O_2NClF$ requires Cl, 20·2%).

4-*Fluoro*-3-*chloronitrobenzene*.—This isomeride was obtained from *p*-fluoronitrobenzene (which was prepared in 33% yield from *p*-nitroaniline by the method described for the *m*-compound) by chlorination in the presence of anhydrous ferric chloride (Rinkes, *Chem. Weekblad*, 1914, **11**, 952). It had m. p. 41·5°.

o-*Fluorochlorobenzene* was prepared from the second of the above nitro-derivatives by elimination of the nitro-group according to

Rinkes's method (*loc. cit.*). 4-Fluoro-3-chloroaniline (m. p. 44°) was obtained without difficulty (yield 90%). The base (16 g.), suspended in concentrated hydrochloric acid (100 c.c.) at − 5°, was diazotised with a solution of sodium nitrite (10 g.) in water (15 c.c.), and the solution cautiously treated below 0° with one of stannous chloride (60 g.) in concentrated hydrochloric acid (50 c.c.), with efficient mechanical stirring. Thirty minutes after the addition was complete the hydrazine hydrochloride was collected and decomposed with cold sodium hydroxide solution. The hydrazine was extracted with ether and obtained as a brown solid (12 g.), but attempts to purify it by crystallisation failed owing to its tendency to autoxidation. It was therefore dissolved in the minimal amount of 75% acetic acid, and the solution added drop by drop to a boiling solution of crystallised cupric sulphate (50 g.) in water (150 c.c.). Nitrogen was evolved and the solution on distillation yielded *o*-fluorochlorobenzene (6·5 g.) as an almost colourless oil, b. p. 138—140°/758 mm.

Nitration of o-*Fluorochlorobenzene.*—*o*-Fluorochlorobenzene (5·0 g.) was added during 1 hour through a capillary tube to nitric acid (15 g., *d* 1·49) at 0°, and the stirring of the mixture was continued for a further 3 hours at the same temperature. The product was extracted with ether, after addition of ice (50 g.) and aqueous sodium hydrogen carbonate (slight deficit), and distilled. Allowing for the small amounts of unchanged *o*-fluorochlorobenzene (b. p. 37°/16 mm.) which were always recovered, the yields of mononitro-derivatives, b. p. 113°/16 mm., 114°/18 mm., 118—119°/26 mm., ranged from 91% to 98%. Repetition of the purification, followed by determinations of the freezing point and labile halogen (see below) showed that the losses were mainly mechanical and that the change of composition during isolation was certainly not more than 1% (Found : N, 7·9. $C_6H_3O_2NClF$ requires N, 8·0%). The nitration product is a very pale yellow solid at the ordinary temperature, and it is possible to separate pure 4-fluoro-3-chloronitrobenzene from it by crystallisation from methyl alcohol.

Action of Sodium Methoxide on the Isomeric Fluorochloronitrobenzenes and on the Nitration Product of o-*Fluorochlorobenzene.*—About 1 g. of the nitro-compound or mixture of nitro-compounds, dissolved in methyl alcohol (100 c.c.) containing 15 mols. of sodium methoxide, was heated at 80° for 60 hours, and the product poured into chloride-free water. Attempts to estimate the loss of alkalinity by titration were not entirely satisfactory owing to the masking of the end-point by the yellow colour of the solution. The solution was nearly neutralised with halogen-free nitric acid, made definitely alkaline with 2 c.c. of 2*N*-sodium carbonate, evaporated to remove

the methyl alcohol, and extracted with ether. The extract was washed with water, and the fluoride and chloride were then estimated in the combined aqueous solutions.

4-Fluoro-3-chloronitrobenzene (0·8947 g.) gave calcium fluoride (0·1972 g., corr.) corresponding to 99·5% of labile fluorine; but 7·0% of the value represents the correction for the solubility of calcium fluoride in water and in the dilute acetic acid used to wash it. The chloride estimation represented 1·3% of labile chlorine, and blank experiments indicated that this figure was real and not due to chloride in the reagents or apparatus. The ethereal extract was not examined.

3-Fluoro-4-chloronitrobenzene gave fluoride and chloride corresponding to 47·3% and 100·0% of labile fluorine and chlorine respectively. A large proportion of the fluorine in this *m*-fluoronitro-compound is therefore ejected from the molecule under the conditions used. For this reason, and also because the accuracy of the fluoride estimation is impaired by the considerable solubility of calcium fluoride (above), we decided to use chloride estimations for the analysis of the nitration product. The ethereal extract on evaporation yielded a yellow solid, which, after crystallisation from methyl alcohol, was identified as 4-nitroveratrole by direct comparison and a mixed m. p. determination with a specimen prepared by Vermeulen's method (*Rec. trav. chim.*, 1906, **25**, 24).

The products of the nitration experiments gave the following percentages of labile chlorine: (1) 22·41, (2) 22·74, (3) 22·07, (4) 22·72 (mean, 22·49%). Three estimations, carried out at the same time and in the same way, of the labile chlorine in the 4-fluoro-3-chloro-isomeride gave (α) 1·13, (β) 1·04, (γ) 1·36% (mean 1·17%). It is shown below that the nitration product of *o*-fluorochlorobenzene is essentially a mixture of 3-fluoro-4-chloro- and 4-fluoro-3-chloro-compounds and contains only a small proportion of the vicinal isomerides. We therefore feel justified in applying to the two *m*-chloronitro-compounds taken together, the small correction (1·17%) determined on the principal member of the pair. Hence it follows that: Orientation by F/Orientation by Cl = 78·68%/21·32%.

Freezing Points of Mixtures of the Isomeric Fluorochloronitrobenzenes and of the Nitration Product of o-*Fluorochlorobenzene*.—In the following table *p* denotes the percentage of 4-fluoro-3-chloronitrobenzene in a mixture with 3-fluoro-4-chloronitrobenzene, and *t* represents the uncorrected freezing point:

p	0·0	10·0	21·1	28·7	34·8	40·5	45·9	51·0	56·2
t	60·0°	55·3°	49·1°	45·0°	41·1°	37·1°	33·0°	26·8°	24·8°
p	59·8	64·1	66·6	71·9	75·4	81·0	87·4	92·2	100·0
t	22·7°	24·7°	26·3°	29·2°	31·1°	34·0°	37·0°	39·1°	42·1°

These points lie on a two-branch diagram, with the eutectic point at $p = 59{\cdot}5\%$ and $t = 22{\cdot}1°$.

The next table refers to the product of the second nitration experiment; x represents the parts of 4-fluoro-3-chloronitrobenzene and y the parts of 3-fluoro-4-chloronitrobenzene added to 100 parts of the nitration product. The freezing points (t) were determined with the same thermometer and apparatus and under the same conditions as those recorded in the previous table.

x	0·0	20·2	72·5	0·0	0·0	0·0	0·0	0·0
y	0·0	0·0	0·0	16·0	24·5	32·8	49·3	63·1
t	28·3°	31·0°	34·8°	22·8°	21·4°	24·5°	28·8°	31·3°

These values lie on a two-branch curve with a eutectic point at 20·7°, and thus show that the depression of the eutectic temperature of the 4-fluoro-3-chloro- and 3-fluoro-4-chloro-compounds caused by the presence of vicinal isomerides in the nitration product is 1·4°. If the first point be placed at the correct temperature on the appropriate branch of the binary diagram, that branch fits accurately, but the second branch is displaced to an extent indicated by a displacement in apparent composition of the eutectic mixture amounting to 2·3% in the direction of the 3-fluoro-4-chloro-isomeride.

A corresponding investigation of the third nitration product gave the following data:

x	0·0	184·1	0·0	0·0	0·0	0·0
y	0·0	0·0	20·4	28·0	33·1	47·5
t	29·0°	35·7°	22·4°	22·2°	24·1°	28·6°

The eutectic point is at 20·9°, so that the depression of the binary eutectic temperature is 1·2°. If the first point is fitted to the binary diagram, the apparent displacement in composition of the eutectic mixture is 2·0% towards the 3-fluoro-4-chloro-compound.

It is evident from these results that, although the nitration products do not accurately behave as binary mixtures of 4-fluoro-3-chloro- and 3-fluoro-4-chloro-nitrobenzenes, they can hardly contain more than a few units % of either of the vicinal isomerides.

We wish to thank the Chemical Society and the Royal Society for defraying part of the cost of this investigation, and the Department of Scientific and Industrial Research for a maintenance grant to one of us.

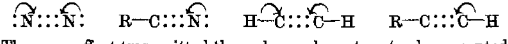
THE UNIVERSITY, LEEDS. [*Received, December 14th, 1927.*]

LVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXIV. The Directive Action in Aromatic Substitution of Certain Groups containing Triple Linkings.*

By JOHN WILLIAM BAKER, KENNETH ERNEST COOPER, and CHRISTOPHER KELK INGOLD.

LANGMUIR has suggested that in the nitrogen molecule the two atomic nuclei and two electrons in addition to the K-electrons are enclosed within a single octet (*J. Amer. Chem. Soc.*, 1919, **41**, 903). This may be regarded as a special form, applied to certain examples (N_2,CO, and CN′), of the following more general principle :—When six valency electrons are mutually shared by two atomic nuclei, the system tends to appropriate two, or four, additional electrons in order to form a stable association of eight, or if possible, of ten, electrons. Usually the appropriation will be incomplete, and it may affect shared or unshared electrons; the limiting special case in which four unshared electrons are completely appropriated corresponds to Langmuir's hypothesis divested of its assumed octet and of its highly particularised stereo-electronic suppositions.

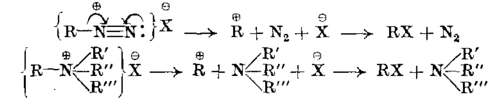
The appropriation of unshared electrons belonging to either or both of the combined atoms will be accompanied by a loss of basic character; the appropriation of shared electrons will confer on the molecule a tendency to ionisation, tautomerisation, etc. Owing to the lability of the unshared electrons in the tervalent nitrogen atom, the effect reaches a maximum when these can be absorbed and hence nitrogen (10*e*-group) and nitriles (8*e*-group) are non-basic, although according to customary electronic formulation they contain the unshared electrons of a tertiary amine. When the electrons required to form a stable 8*e*- or 10*e*-group are shared with hydrogen, the intrinsic tendency of the latter to pass into the cationic condition co-operates in favour of ionisation, and hence in hydrocyanic acid one hydrogen atom, in alkylacetylenes one hydrogen atom, and in acetylene two hydrogen atoms, are replaceable by elements (metals) which, having greater stability in the form of their cations, can become combined by electrovalencies to the organic anion (CN′, RC_2′, C_2″) with minimal disturbance of the stable electron-groups.



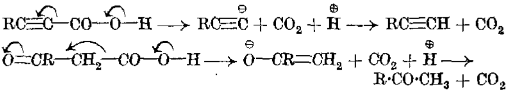
The same effect transmitted through a carbon atom (and augmented by other influences) is observed in nitriles possessing an α-hydrogen atom.

When the shared electrons bind atoms other than hydrogen,

different phenomena may arise. Thus diazonium salts decompose more easily than other quaternary ammonium salts because the quaternary group in the former has an enhanced power of withdrawing electrons from the hydrocarbon radical (compare Hanhart and Ingold, J., 1927, 250) :



To take one other example from the many available, acetylenic acids lose carbon dioxide on heating, whereas olefinic and saturated acids do not unless an electron-sink is present; in fact the decompositions of propiolic acid homologues and β-ketonic acids, etc., are closely comparable :



These conclusions receive independent justification from the experiments recorded below on the orienting influence in aromatic substitution of certain groups containing the triple linking. For example, we find that phenylpropiolic acid on nitration yields as much as 8%, and ethyl phenylpropiolate 6%, of the *m*-derivative, *in contrast with cinnamic acid and its ester, which yield op-products* practically exclusively. We have no hesitation in ascribing this effect to the triple linking, rather than to any greater electron-attraction by the acetylene-bound carboxyl group as compared with the olefin-bound carboxyl group, because the difference of electron strain in the linkings binding the carboxyl groups in the two cases is in the wrong sense. This is shown, not only by the much greater tendency of acetylenic acids to lose carbon dioxide, but also by their much greater strengths as compared with the corresponding olefinic (and saturated) acids :

	$k \times 10^5$.		$k \times 10^5$.		$k \times 10^5$.
n-Butyric acid ...	1·5	α-Crotonic acid	5·6	Tetrolic acid ...	246
β-Phenylpropionic acid ...	2·3	Cinnamic acid ...	8·6*	Phenylpropiolic acid	590

* *Mean of values for ordinary and allo-modifications.*

Hence the electron-attracting power of the acetylenic bond in phenylpropiolic acid is distributed between the two directions, and the *m*-orientation observed represents only a part of the total effect of the group.

No exact estimate of the proportion of *m*-derivative formed on nitration of benzonitrile appears to have been made previously. We find that, on nitration at 0° in nitric acid, 81% of the *m*-nitro-compound is produced. Phenylacetonitrile yields 14% of the *m*-derivative under similar conditions, showing that the *m*-orienting influence of the cyano-group is considerable even when transmitted through an interposed methylene group. The much greater *m*-orienting power of the cyano-group than of the acetylenic group is in accordance with the view (Baker and Ingold, J., 1927, 832) that the electrons mutually shared by C and N in ·C⋮N must be unequally shared, since they will be more under the control of the more powerful atomic nucleus (N), and that the effect of this must be to produce a *m*-orienting dipole. It may be pointed out that the recognition of these superimposed effects in the cyano-radical tends to favour our view that the additional electrons required to form the stable binuclear electron-groups considered are not *shared* (in the ordinary sense) by the two nuclei in the fully formed group. Admittedly this inference relates primarily to the 8*e*-group; but if it were applied to the 10*e*-group it would dispose of Langmuir's binuclear octet.

Finally, it should be remarked that the feeble basicity of azo- and nitroso-compounds (that their basicity is not nil is shown by their conversion into their amine oxides, azoxy- and nitro-compounds by oxidation) requires some extension of the above principles to include certain associations of two nuclei having originally four mutually shared and four unshared electrons. The facile elimination of nitrogen from dihydropyrazoles and aliphatic azo-compounds is a further indication in the same direction, and the fact that this reaction does not readily occur with aromatic azo-compounds is illuminated by reference to the analogous decomposition of diazonium salts. Here the presence of the positive charge, and the greater stability of the 10*e*-group originating in six shared electrons, render the series more labile as a whole, but the above mechanism of decomposition necessitates that the stability of an individual of the series $\{RN_2\}^{\cdot}X'$ should depend on the power of the variable radical R to hold electrons; hence, stability diminishes in the series $NO_2{\cdot}C_6H_4$–$>C_6H_5$–$>CH_3{\cdot}C_6H_4$–$>$ ······ $>$alphyl–. In azo-compounds RN_2R', the stability should be higher throughout, but should nevertheless be least when R = alphyl.* These consider-

* In "mixed" azo-compounds the group which most readily parts with electrons will determine the decompostion: *e.g.*, CPh_3—N=N→Ph ⟶ $CPh_3^{\oplus} + N_2Ph^{\ominus} \longrightarrow CPh_3^{\oplus} + N_2 + Ph^{\ominus} \longrightarrow CPh_4 + N_2$ (Gomberg and Berger, *Ber.*, 1903, **36**, 1090).

ations raise the question whether the large electron affinity of the carbonyl group is not partly attributable to the cause indicated.

A consideration of the stabilities of the compounds mentioned appears to show that 2 electrons in the 10e-group are *less* firmly bound than the remaining 8. This is the reverse of Langmuir's idea, and presumably has implications relating to the spectroscopy of nitrogen and cyanogen (it may not apply to acetylene).

EXPERIMENTAL.

(A) *Acetylene Derivatives.*

(i) *Nitration of Phenylpropiolic Acid.*—This substance can be nitrated quantitatively, but the reaction requires very careful control and is best performed on a small scale in thin-walled test-tubes cooled in a bath of liquid ammonia. The acid (1·023 g.) was added during 15 minutes in very small portions with rapid mechanical stirring to 15 g. of freshly distilled absolute nitric acid at a temperature slightly below $-30°$. After a further 15 minutes the solution was poured into ice and water, and the nitro-acids were extracted with much ether. The extract was evaporated, the evaporation being almost completed at the ordinary temperature, and the residue, which contained nitric acid, was repeatedly mixed with a little water and nearly dried over potassium hydroxide in a vacuum desiccator, and was finally dried until the weight became constant (yield 1·35 g. = theoretical) (Found: C, 56·4; H, 2·9. Calc.: C, 56·5; H, 2·6%). On oxidation with boiling permanganate at low concentration, nitrobenzoic acids were obtained in 85% yield; *p*- and *m*-nitrophenylpropiolic acids under the same conditions yielded the corresponding nitrobenzoic acids in 85% and 88% yield respectively. The mixed nitrobenzoic acids contained *para* 65·0%, *meta* 8·0% (benzoic acid, *nil*). Hence the proportion of *m*-nitrophenylpropiolic acid formed on nitration is 7·7% (rounded to 8% in the introduction). *Ortho*, by difference, 27%.

(ii) *Nitration of Ethyl Phenylpropiolate.*—This experiment was carried out like the preceding one, excepting that the mixture formed on pouring the nitric acid solution into ice-water was made alkaline with sodium carbonate before being extracted with ether. The apparent yield of nitrophenylpropiolic esters was 90%, but this contained 3% of un-nitrated material (below). The aqueous solution was acidified and treated in accordance with the description given above for the isolation of nitrophenylpropiolic acids, 10% of which was obtained, accounting for the rest of the material. The bulk of the ethyl *p*-nitrophenylpropiolate (51·8%) was readily separated in a pure condition by crystallisation from methyl alcohol;

and the remaining mixture was oxidised (yield 96%) to nitrobenzoic acids by means of very dilute permanganate. The mixed acids contained benzoic acid (estimated by sublimation at 100°) equivalent to 3·0% of un-nitrated ethyl phenylpropiolate. After separating the nitrobenzoic acids and applying the usual corrections, including one for the material which had escaped nitration, we obtained *para* 57·9%, *meta* 6·1%, *ortho* (by difference) 36·0%, and it does not affect the rounded proportion of *meta*- (6%) whether the 10% of hydrolysis occurred before or after nitration.

We had hoped to include in this communication an account of the nitration of phenylacetylene and tolane, but in spite of many attempts we have not yet succeeded in establishing suitable conditions for the quantitative nitration of these substances.

(B) *Nitriles.*

(i) *Nitration of Benzonitrile.*—The benzonitrile was run very slowly from a weight-pipette into 15 parts of well-stirred absolute nitric acid at 0°, and the mixture was kept at this temperature for a further 2·5 hours. It is essential that no rise of temperature should occur, since otherwise the hydrolysis becomes perceptible. After admixture with ice-water and sufficient potassium carbonate the nitro-nitriles were extracted with ether (yield quantitative). There was no acid product. In the first of the three experiments, the results of which are recorded below, 23·8% of pure *m*-nitrobenzonitrile was separated by crystallisation from ligroin, and the remaining mixture was hydrolysed by boiling for 16 hours with 50% (by weight) sulphuric acid, a process which was quantitative both in this instance and in preliminary experiments on the separate isomerides. In the second and third experiments the whole product was quantitatively hydrolysed without preliminary separation. As in the cases of benzamide, benzoic acid and benzoyl chloride (Cooper and Ingold, J., 1927, 836) the proportion of *p*-isomeride is of the order of the correction for the solubility of *p*-nitrobenzoic acid in chloroform and we cannot assign a definite figure to it; the chief by-product is *o*-nitrobenzonitrile. For the *m*-isomeride we obtained (i) 80·0%, (ii) 80·0%, (iii) 81·6%. Mean, 80·53% (given as 81% in the introduction).

Nitration of Phenylacetonitrile.—Salkowski has shown (*Ber.*, 1884, **17**, 507) that the meta-isomeride is formed in the nitration of this substance, but his method did not enable us to estimate the proportion. We used the method of hydrolysis and subsequent oxidation to nitrobenzoic acids, supplemented by comparative experiments with the separate isomerides. For this purpose *o*-nitrophenylacetonitrile was prepared by Bamberger's method

(*Ber.*, 1886, **19**, 2635). The *m*-isomeride was obtained by Heller's method (*Annalen*, 1908, **358**, 357), but in the purification of the product it was found advisable to distil the crude oil obtained by extraction with benzene; the unchanged *m*-nitrobenzyl chloride distilled first at 155—160°/3 mm., and the cyanide at about 180°/3 mm. It was still impure (m. p. 50—55°) and was therefore crystallised from dry ether, in which the cyanide is sparingly soluble and the chloride easily soluble (m. p. 61°). The *p*-isomeride was obtained by nitrating phenylacetonitrile and crystallising the product from alcohol.

Phenylacetonitrile was slowly added to 15 parts of nitric acid (*d* 1·49) at − 10° to − 15°, and the product was mixed with ice, nearly neutralised with dilute sodium hydroxide solution, and made alkaline with sodium hydrogen carbonate. The crystalline product was collected, washed, and dried (yield 86·8%), and the filtrate was extracted with ether (yield 11·2%); total yield 98% (Found: C, 59·1; H, 3·8. Calc.: C, 59·3; H, 3·7%). The main fraction on crystallisation from alcohol yielded 62·6% of pure *p*-nitrophenylacetonitrile; the residues and the extracted fraction were oxidised separately, and the nitrobenzoic acids separated as usual. In another experiment (yield 98·5%) the whole product was hydrolysed and the nitrophenylacetic acids were oxidised to nitrobenzoic acids (yield 89%), which were separated. Comparative experiments with *o*-, *m*- and *p*-nitrophenylacetonitriles gave the appropriate nitrobenzoic acids in 85%, 80% and 86% yields respectively, from which we conclude that the alteration in the proportion of isomerides which takes place when a mixture of nitrophenylacetonitriles is hydrolysed and oxidised under the conditions employed is inconsiderable. The results of the two experiments were as follows: *ortho*, 16·5, 17% (by difference); *meta*, 14·5, 14%; *para*, 69, 69%.

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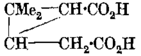
THE UNIVERSITY, LEEDS. [*Received, December 14th*, 1927.]

LIX.—α-*iso*Propylglutaconic Acid.

By KALVOI VENKATAKRISHNA HARIHARAN, KOTTIAZATH NARAYANA MENON, and JOHN LIONEL SIMONSEN.

AMONGST the products formed when *d*-Δ^3-carene was oxidised with potassium permanganate in acetone solution was an acid, $C_8H_{12}O_4$, which was probably *cis*-homocaronic acid (I). The acid was,

however, somewhat readily attacked by potassium permanganate in alkaline solution and also showed certain other anomalous properties which made it doubtful whether it possessed this constitution. In describing the acid (J., 1923, **123**, 553) the cyclic structure was only advanced with reserve and it was suggested that the acid might be either α- or β-*iso*propylglutaconic acid (II or III).

(I.) 

$$CO_2H{\cdot}C(CHMe_2){:}CH{\cdot}CH_2{\cdot}CO_2H \quad \text{(II.)}$$

$$CO_2H{\cdot}CH{:}C(CHMe_2){\cdot}CH_2{\cdot}CO_2H \quad \text{(III.)}$$

The syntheses of cis- and trans-α-iso*propylglutaconic acids* (II) are now recorded together with an account of an unsuccessful attempt to synthesise *cis*-homocaronic acid. β-*iso*Propylglutaconic acid also has been prepared in small quantity and will be described *in a future paper. None of the glutaconic acids is identical with the* acid obtained from *d*-Δ^3-carene.

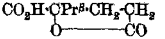
α-*iso*Propylglutaconic acid might be synthesised (1) directly by the condensation of ethyl sodiodicarboxyglutaconate with *iso*propyl iodide, (2) and (3) by the removal of a halogen acid from the α- or β-monohalogen derivative of ethyl α-*iso*propylglutarate. Only method (3), however, leads to the required acid.

Although α-methylglutaconic acid (Feist and Pomme, *Annalen*, 1909, **370**, 63) and α-ethylglutaconic acid (Gutzeit and Dressel, *Ber.*, 1890, **23**, 182) have been prepared from ethyl sodiodicarboxyglutaconate and the appropriate alkyl iodide, the sole product of the interaction of the sodio-compound and *iso*propyl iodide under the conditions given on p. 434 was ethyl trimesate. The formation of this ester by the condensation of derivatives of ethyl glutaconate, such as ethyl α-formylglutaconate, has been repeatedly observed (von Pechmann, *Annalen*, 1893, **273**, 174; Wislicenus and Bindemann, *ibid.*, 1901, **316**, 34) and presumably ethyl α-*iso*propylglutaconate, which must have been formed as a primary product of the reaction, underwent a similar condensation.

The bromination of α-*iso*propylglutaryl chloride did not proceed smoothly. A bromo-ester of constant boiling point and correct composition could not be isolated. Although a small excess of bromine was used, the reaction mixture, after being poured into alcohol, contained a large amount of ethyl *iso*propylglutarate, and the main product was an acid ester; this on treatment with

$$CO_2R{\cdot}CBrPr^{\beta}{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2R$$

(IV; R = H or Et.)



(V.)

alkali gave γ-hydroxy-β-methylpentane-γε-dicarboxylic acid, which was isolated as the lactone (V) (compare Fittig and Wolff, *Annalen*,

1895, **288**, 189). This lactone was obtained in an almost theoretical yield on treatment with alkali of the acid products obtained by the esterification of the bromo-acid chloride and it follows, therefore, that it was a tertiary hydrogen atom in the α-*iso*propylglutaryl chloride which had been substituted, yielding α-bromo-α-*iso*propylglutaryl chloride. This result is somewhat remarkable, since it was shown by Ingold (J., 1925, **127**, 392) that the main product of the bromination of α-methylglutaryl chloride was γ-bromo-α-methylglutaryl chloride, only very little of the α-bromo-compound being formed. Apart from α-*iso*propylglutaric acid and the above-mentioned lactone we were not able to isolate any homogeneous products from our reaction, although it is probable that the glutaconic acid was formed, since some of the fractions of the liquid acids obtained after removal of hydrogen bromide were unstable to potassium permanganate. The quantity obtained was insufficient for purification.

Ethyl β-*chloro*-α-iso*propylglutarate* (VIII) was readily prepared by the reactions indicated in the following scheme :

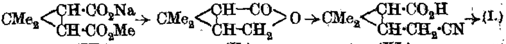
$$CO_2Et{\cdot}CHPr^{\beta}{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et \rightarrow CO_2Et{\cdot}CHPr^{\beta}{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2Et \rightarrow$$

(VI.) (VII.)

$$\text{(VIII.)}\ CO_2Et{\cdot}CHPr^{\beta}{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2Et \longrightarrow \text{(II.)}$$

Ethyl α-iso*propylacetonedicarboxylate* (VI) was obtained in an excellent yield when ethyl potassioacetonedicarboxylate was treated with *iso*propyl iodide in alcoholic solution. It could not be reduced catalytically to the *hydroxy-ester* (VII), which could only be prepared by prolonged reduction with a large excess of sodium amalgam. The preparation of the chloro-ester and its conversion into the glutaconic acid (II) were readily carried out under conditions similar to those used by Perkin and Tattersall (J., 1905, **87**, 362). Separation of the *cis*- and *trans*-forms of the acid was effected by means of acetyl chloride (Thole and Thorpe, J., 1911, **99**, 2227).

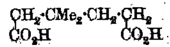
For the synthesis of homocaronic acid the most ready method appeared to be that represented by the scheme :



(IX.) (X.) (XI.)

When sodium methyl caronate (IX) was reduced with sodium and alcohol, a small quantity of a neutral oil was obtained. This

(XII.)

 (XIII.)

was, not (X), but the lactone of δ-hydroxy-ββ-dimethylvaleric acid (XII) (Blanc, *Bull. Soc. chim.*, 1905, **33**, 897), since on treat-

ıent with potassium cyanide at 275°, followed by hydrolysis of the esulting nitrile, it gave ββ-dimethyladipic acid (XIII). The eduction of the ester group had therefore been accompanied by ission of the *cyclo*propane ring. Further experiments on the ynthesis of homocaronic acid are in progress.

EXPERIMENTAL.

The Condensation of Ethyl Sodiodicarboxyglutaconate and iso-*Propyl Iodide: Ethyl Trimesate.*—A mixture of the dry sodio-derivative (7 g.), alcohol (10 c.c.), and *iso*propyl iodide (4 g.) was heated in a sealed tube at 140—160° for 4 hours. Considerable pressure was developed and the liquid contained a colourless solid. This was collected and well washed with alcohol; it proved to be a nixture of ethyl trimesate and sodium carbonate. The filtrate, after removal of the alcohol, was dissolved in ether to remove inorganic matter, the ether evaporated, and the residual oil distilled under diminished pressure (17 mm.); about half passed over at 100—110°, and the remainder at 205—225°. The higher-boiling fraction slowly crystallised in needles, m. p. 125—127° (after draining on porous porcelain), 132—133° (constant; after recrystallisation from alcohol). The substance was identified, by analysis (Found: C, 61·3; H, 6·3. Calc.: C, 61·2; H, 6·1%) and by direct comparison with an authentic specimen, as ethyl trimesate. The lower-boiling oil was a mixture and owing to the small quantity available was not further examined.

Bromination of α-iso*Propylglutaryl Chloride.*—α-*iso*Propylglutaric acid was most conveniently prepared by the hydrolysis with 50% sulphuric acid of *ethyl* α-*cyano*-α-iso*propylglutarate*, which was obtained in an excellent yield under the following conditions: Ethyl *iso*propylcyanoacetate (38 g.) was added to a solution of sodium (5·6 g.) in alcohol (75 c.c.) and to the mixture, cooled in salt and ice, ethyl β-iodopropionate (63·7 g.) was gradually added, care being taken that the temperature did not rise above 0°. After remaining at 0° for 5 hours, the reaction mixture was kept at room temperature over-night and finally heated on the water-bath for 1 hour. The condensation product was separated in the usual manner and distilled under diminished pressure, practically the whole distilling at 195°/32 mm. (yield, 75%) (Found: N, 5·7. $C_{13}H_{21}O_4N$ requires N, 5·5%). It was a somewhat viscid, yellow oil with a faint but unpleasant smell.

α-*iso*Propylglutaric acid (45 g.) was mixed with phosphorus pentachloride (110 g.) and, after the formation of the acid chloride was complete, dry bromine (44 g.) was gradually added; the mixture was then heated on the water-bath for 24 hours, only the slight

excess of bromine remaining unabsorbed. The acid chloride was poured into well-cooled alcohol and next day ice was added. The heavy oil precipitated was dissolved in ether, and the ethereal solution was well washed with sodium carbonate solution (*A*), dried, and evaporated. After repeated fractionation under diminished pressure (30 mm.), four fractions were separated: (i) 130—145°, (ii) 145—165°, (iii) 165—180°, and (iv) 180—210°. Fractions (i) and (ii) contained only traces of bromine, and fractions (iii) and (iv), which were small in quantity, contained 13·5 and 23·3% of bromine respectively ($C_{12}H_{21}O_4Br$ requires Br, 27·5%).

Fractions (i) and (ii) were examined separately and gave identical products. After hydrolysis with alcoholic potassium hydroxide solution and separation of the organic acid in the usual manner, an oil was obtained which partly crystallised on keeping. It was converted through the sparingly soluble copper salt into pure α-*iso*propylglutaric acid.

Fraction (iii) was boiled with an excess of freshly distilled diethylaniline. The ester obtained distilled mainly at 155—165°/36 mm.; a small amount of an oil boiled above this temperature. From the main fraction, only α-*iso*propylglutaric acid could be separated after hydrolysis.

Fraction (iv) when treated in a similar manner gave an oil, b. p. 170—200°/30 mm. This gave on hydrolysis a liquid acid which was unstable to potassium permanganate in alkaline solution but was insufficient in quantity for investigation.

The sodium carbonate solution (*A*) on acidification deposited an oil which, after extraction with ether and drying in a vacuum, contained Br, 18·3%. The oil was added to an excess of boiling alcoholic potassium hydroxide solution, the alcohol removed, and the alkaline solution acidified and extracted with ether. On removal of the ether an oil was obtained which crystallised completely on keeping. It was purified by slow evaporation of its benzene solution, crystallising in prisms, m. p. 65—67°. Its identity with the lactone (V) of γ-hydroxy-β-methylpentane-γε-dicarboxylic acid was confirmed by analysis (Found: C, 56·1; H, 7·1; *M*, 171·9. Calc.: C, 55·8; H, 7·0%; *M*, 172).

Ethyl α-iso*Propylacetonedicarboxylate* (VI).—A mixture of ethyl potassioacetonedicarboxylate (32 g.), alcohol (50 c.c.), and *iso*propyl iodide (23 g.) was heated on the water-bath for 6 hours. After addition of water the *ester* was separated by ether and distilled under diminished pressure, the bulk passing over at 141—143°/9 mm. (yield, 60%). For analysis it was redistilled; b. p. 142—143°/9 mm. (Found: C, 59·0; H, 8·3. $C_{12}H_{20}O_5$ requires C, 59·0; H, 8·2%). The ester is a colourless oil of pleasant odour and gives

with ferric chloride a deep red coloration. Its hydrolysis wit alcoholic potassium hydroxide gives α-iso*propylacetonedicarboxyl* *acid*, which crystallises from ether in needles, decomp. 153°, an gradually decomposes on keeping (Found : C, 50·7 ; H, 6·6. $C_8H_{12}C$ requires C, 51·1 ; H, 6·4%).

*Ethyl β-Hydroxy-α-*iso*propylglutarate* (VII).—The preceding ket ester (80 g.) was dissolved in alcohol (200 c.c.) and, after the additic of water until the solution was just turbid, sodium amalgam (5 kg 2½%) was gradually added, the solution being vigorously stirr and a rapid stream of carbon dioxide passed through it. When tl reduction was complete (6 days), the alcohol was removed in stear the unhydrolysed ester (8 g.) separated by ether, and the alkali solution evaporated on the water-bath. The dry residue of sal was heated with alcohol and an excess of sulphuric acid on tl water-bath for 10—12 hours, giving *ethyl β-hydroxy-α-*iso*propy glutarate*, b. p. 145—146°/10 mm. (Found: C, 58·1; H, 9· $C_{12}H_{22}O_5$ requires C, 58·5; H, 8·9%), as a somewhat viscid c which gave no colour with ferric chloride. The hydroxy-ac obtained by hydrolysis could not be crystallised.

*Ethyl β-Chloro-α-*iso*propylglutarate*.—To the well-cooled hydrox ester (13 g.), phosphorus pentachloride (11·5 g.) was gradual added. It slowly dissolved and on allowing the temperature t rise hydrogen chloride was evolved; reaction was complete at 5 after 30 minutes. The cooled mixture was poured on ice, tl chloro-ester separated by ether, and the ethereal solution washe with sodium carbonate solution, dried, and evaporated. The est had a penetrating smell and was analysed after being kept for son days in a vacuum (Found : Cl, 12·2. $C_{12}H_{21}O_4Cl$ requires Cl, 13·4%

*Ethyl α-*iso*Propylglutaconate*.—The chloro-ester (19 g.) was mixe with freshly distilled diethylaniline (50 g.) and heated at 180—19 for 12 hours. The cooled mixture was poured on ice and dilu hydrochloric acid, the oil dissolved in ether, and the ethereal extra well washed with dilute hydrochloric acid and with sodium carbona solution, dried, and evaporated. After two distillations an o was obtained, b. p. 148—150°/15 mm. As the ester containe traces of chlorine, it was not analysed.

cis- *and* trans-*α-*iso*Propylglutaconic Acids* (II).—The ester (24 g was hydrolysed with methyl-alcoholic potassium hydroxide an after removal of the alcohol the acid was separated from the acidifie solution by repeated extraction with ether; on removal of tl solvent, an oil was obtained which partly solidified on keepin (yield 16 g.). The crude acid, m. p. 80—100°, was a mixture of th *cis*- and *trans*-forms, which were separated by treatment with acet

The acid (26 g.) was mixed with acetyl chloride (100 g.) and heated on the water-bath until all evolution of hydrogen chloride ceased (8 hours). The excess of acetyl chloride was removed under diminished pressure, and the deep red reaction mixture poured into an ice-cold solution of sodium bicarhonate. The neutral oil (A) was extracted with ether, the alkaline solution being reserved.

The ethereal solution of (A) gave on removal of the solvent a deep red oil having a pungent smell and evidently consisting of the chloro-anhydride. On treatment with potassium hydroxide solution it rapidly dissolved and a sparingly soluble *potassium* salt was deposited in colourless leaflets which became green, brown, and finally red. It was recrystallised from alcohol (Found: K, 19·7. $C_8H_9O_3K$ requires K, 20·3%). When an aqueous solution of the potassium salt was acidified with dilute acetic acid an oil was deposited which could not be induced to crystallise and probably consisted of the hydroxy-anhydride. The oil in neutral solution gave with silver nitrate a black precipitate, and, as has been previously observed in similar cases, in alkaline solution it became deep red on keeping.

For the preparation of the *cis*-modification of the acid the above-mentioned potassium salt was dissolved in water and digested with an excess of potassium hydroxide solution. From the acidified solution, repeated extraction with ether removed the acid, which was obtained as an oil and rapidly crystallised. It was recrystallised from cold dilute hydrochloric acid (Found: C, 55·4; H, 7·3; *M*, 173. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%; *M*, 172).

cis-α-iso*Propylglutaconic acid* separated from hydrochloric acid in small plates, m. p. 101°, softening slightly at 95°. The acid was readily soluble in water, chloroform, and benzene, more sparingly soluble in light petroleum. The calcium and barium salts are readily soluble in water, but an aqueous solution of the acid gave on addition of copper acetate a sparingly soluble copper salt. In acetic acid solution the acid does not take up bromine, but its alkaline solution immediately decolorises potassium permanganate.

The sodium bicarbonate solution, from which the chloroanhydride had been separated, was acidified, and the acid extracted with ether. On evaporation of the ether an oil remained which on keeping partly solidified. After draining on porous porcelain the acid was purified by crystallisation from either water or chloroform (Found: C, 56·2; H, 7·0. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%).

trans-α-iso*Propylglutaconic acid* separated from chloroform in feathery needles, m. p. 132°. It was somewhat sparingly soluble in cold water, chloroform, and benzene, readily soluble in these solvents when hot, and very sparingly soluble in light petroleum.

The barium salt crystallised from water in small plates. The acid resembles the *cis*-form in its behaviour towards bromine and potassium permanganate.

Reduction of the Monomethyl Ester of Caronic Acid.—For the preparation of the monomethyl ester, caronic anhydride (7 g.) was added all at once to a solution of sodium (1·15 g.) in methyl alcohol (50 c.c.). After removal of the alcohol the sodium salt was dissolved in water and the solution acidified; an oil then separated which crystallised on scratching. It separated from benzene–ligroin in short prisms, m. p. 108—110° (Found: C, 55·6; H, 7·1. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%).

For the reduction of the acid ester the sodium salt (30 g.) was dissolved in alcohol (350 c.c.) and added as rapidly as possible to sodium (36 g.), kept in a boiling water-bath. Owing to the separation of the sodium salt the whole mass became pasty. The alcohol was removed in steam, the aqueous solution acidified and repeatedly extracted with ether, and the ether dried and evaporated. The crystalline residue was distilled in steam, a small quantity of an oil passing over. This was extracted with ether and after the removal of the solvent the residual oil (2 g.) was distilled; b. p. 137°/43 mm., 232—235°/685 mm. On cooling in ice–salt the distillate crystallised, but it melted at room temperature and was evidently not quite pure. The lactone was converted into the dibasic acid by the method of Blanc (*loc. cit.*) and this acid was identified as ββ-dimethyladipic acid by its m. p. (86°) and by analysis (Found: C, 55·0; H, 8·3. Calc.: C, 55·1; H, 8·0%).

THE INDIAN INSTITUTE OF SCIENCE,
BANGALORE. [*Received, December 12th, 1927.*]

LX.—*Hydrogenation of Cyclic Compounds under Pressure in Presence of Osmium and Other Catalysts.*

By V. S. SADIKOV and A. K. MIKHAILOV.

WHEN certain cyclic compounds (*e.g.*, benzene, naphthalene, pyridine, quinoline) were hydrogenated under pressure in Ipatiev's apparatus, it was found that the rate of absorption of the gas was dependent upon both the temperature (exhibiting a definite optimum) and the type of catalyst, particularly when platinum, palladium, iridium, or osmium was used on a supporting substance such as asbestos. Moreover, the concentration of the metal on the surface affected the rate of reaction.

We have therefore made comparative measurements of the effects of the above metals on the hydrogenation of pyridine and quinoline under pressure, and have also studied a number of subsidiary factors.

The efficiency of a given catalyst may be assessed according to the rate of the reaction, *i.e.*, from the quantity of hydrogen absorbed during equal intervals of time. As the reactions only proceed within certain temperature limits, the volumes have to be read at high temperatures (250—320°) and are therefore affected not only by thermal expansion but also by the partial pressures of other substances. The total amounts of hydrogen absorbed as shown by the manometer (at room temperature) therefore differ according to the temperature of the bomb; nevertheless the rate of decrease of hydrogen pressure at a definite optimal temperature was sufficiently well defined to enable the reaction to be followed and also to indicate certain peculiarities in the catalysts.

EXPERIMENTAL.

50 G. of the substance under investigation are placed in a glass tube, and on the surface of the liquid is placed a plug containing the catalyst (6 g. of asbestos coated with the metal), the plug being kept in position by means of a copper net. The tube is then put into the Ipatiev apparatus, which is closed and filled with hydrogen up to a pressure of about 100 atm. After the valve has been shut, the apparatus is allowed to stand for several hours in order to ensure that it is air-tight, as judged by the constancy of the manometer reading, and then heated to the optimal temperature, which should by determined by means of preliminary tests and is usually about 80° above the boiling point of the substance being hydrogenated. The experiment is considered as beginning only when the changes in the manometer readings have reached their maximal value within the given optimal temperature range, such readings being taken every 15 minutes. Usually the experiment was continued on several successive days, being interrupted over-night; it was regarded as being completed when the decrease of pressure became negligible.

Hydrogenation under such conditions differs somewhat from that in an open tube, as in Sabatier and Senderens's method, and also from that under pressure, as in Ipatiev's method. In our experiments, the catalytic mass is not distributed throughout the liquid (as in the latter method of Ipatiev), but forms a separate layer, penetrated both by the vapour of the liquid undergoing hydrogenation and by the hydrogen. Such conditions are favourable in that they prolong the time during which the substance is kept within the contact zone and also secure intimate contact. Thus,

the necessity of mechanically intermixing the liquid with the catalyst is avoided. Hydrogenation is effected in the vapour phase, as in the Sabatier process, but also under pressure, as in Ipatiev's process. Such a combination is rendered still more effective if the low-boiling products are condensed in a subsidiary apparatus such as will be described in a later paper.

Preparation of Catalysts.—Osmium–asbestos. Washed and ignited asbestos (asbestos cotton) is shaken into a pulp with water and an aqueous solution of the required amount of osmium tetroxide is added, followed by solutions of sodium hydroxide and hydrazine hydrochloride until the liquid is completely decolorised; the whole is then heated in the water-bath to secure precipitation of metallic osmium upon the asbestos, which is drained, well washed in hot water, and dried first at 70—80° and finally in a vacuum desiccator over phosphoric anhydride.

Osmium–cerium–asbestos. A solution of osmium tetroxide and cerium nitrate in the required ratio is poured over asbestos pulp, and a small quantity of ammonia and 1 c.c. of hydrogen peroxide for every 0·1 g. of cerium salt are added. The whole is then boiled with solutions of caustic potash and hydrazine hydrochloride and treated as before.

Activation of Catalysts.—The catalyst may undergo an alteration in its degree of dispersion owing to the temperature employed, or it may become enveloped by difficultly volatile by-products of the reaction, or, further, its efficiency may be impaired in consequence of the oxygen of the oxides becoming involved in organic complexes; such occurrences may cause either a definite poisoning of the catalyst or a temporary fatigue. After a certain time, or after having transformed a definite quantity of substance, the catalyst therefore requires artificial reactivation, which may be effected by supplying it with oxygen for the purpose of forming an active surface rich in oxides. This may be accomplished either by heating it at 400° in a current of oxygen, or by subjecting it to the action of hydrogen peroxide at room temperature, the latter procedure being preferable as causing less disturbance in the state of dispersion: the catalyst is put into water, a few c.c. of hydrogen peroxide are added and rapidly drained off, and the catalyst is dried in the desiccator. The presence of a certain amount of water in the catalyst often increases its activity, so that, alternatively, drying may be effected at 105°. Any traces of organic matter are removed from the surface of the mass by thorough extraction with alcohol or ether in a Soxhlet apparatus.

Curves 1, 2, and 3 (Fig. 1) illustrate the hydrogenation of quinoline in presence of 20% platinum on asbestos at 320°: the fall

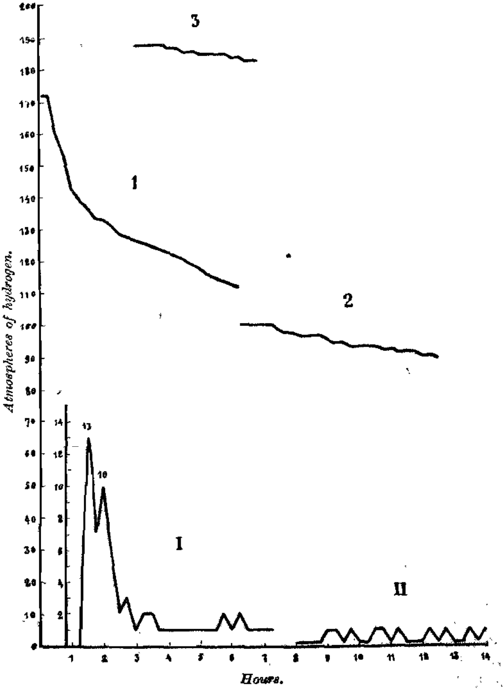
TABLE I.

Quinoline; 20% Pt on asbestos; 320°.

I. .... 0, 13, 7, 10, 2, 2, 3, 1, 2, 2, 1, 1, 1, 1, 1, 1, 1, 1, 2, 1, 2, 1, 1, 1, 1.
II. .... 0, 0, 0, 0, 1, 1, 0, 1, 0, 0, 1, 1, 0, 1, 0, 0, 0, 1, 0, 1, 0, 0, 1, 0, 1.

Product of reaction: 91% tetrahydroquinoline.

FIG. 1.



of the pressure of hydrogen being measured every 15 min. at 320°. Curve 1 denotes rapid hydrogenation, which quickly slackens owing to fatigue of the catalyst. Table I (I) and Curve I show the amounts of hydrogen absorbed (in atmos.) in successive intervals of 15 mins., and it will be noted that the absorption proceeds discontinnously, the curve showing undulations.

Curve 2 represents the course of hydrogenation after 12 hours' interruption (the bomb having been cooled to room temperature and subsequently re-heated to the optimal temperature of 320°); Table I (II) and Curve II show the successive absorptions and indicate considerable fatigue of the catalyst. On the first heating (I), an absorption equal to 59 atm. occurred during 6¼ hours, whereas during the second heating the amount absorbed for an equal lapse of time only reached 10 atm. Now, in the first case the fluctuations in the quantities of hydrogen absorbed give evidence that periods of fatigue alternate with periods of partial reactivation of the catalysts, and similar renewal of activity may also be observed in the second case where values of 1 atm. alternate with inactivity.

Finally, in the third case (curve 3) a state of extinction of the catalyst is attained, notwithstanding the optimal temperature, the excess of hydrogen re-introduced (188 atm.), and the incomplete hydrogenation of the quinoline (only 91% of tetrahydroquinoline).

20% Palladium–asbestos produces a more uniform and extensive hydrogenation of quinoline. After a short induction period (15 minutes), at the optimal temperature, absorption starts and soon attains a maximum of 5 atm. in 15 mins., followed by oscillations from 3 to 2 atm. in 15 mins.; thus, during the first hour 15 atm. were absorbed, whilst in the course of the following 4½ hours the absorption was only 6·9 atm. per hour. Heating anew after cooling gave an absorption of 3 atm. per hour (21 atm. in 7 hours). These two ranges gave the following values for absorption in successive periods of 15 mins.:

I. ... 0, 4, 5, 3, 3, 3, 1, 2, 2, 3, 3, 2, 1, 0, 2, 3, 1, 1, 2, 1, 1, 1, 2.
(5¾ hours; 46 atm.)

II.... 0, 0, 1, 2, 1, 0, 0, 1, 1, 1, 1, 1, 1, 0, 0, 1, 1, 2, 0, 1, 0, 1, 0, 1, 1, 1, 1, 1.
(7 hours; 21 atm.)

The powerful catalytic effect of osmium, which is effective in a concentration of only 1% on asbestos, is due to the ease of formation of its oxide in contact with the air, or when exposed to the action of hydrogen peroxide. With the above concentration at 320°, the following ranges were obtained for the hydrogenation of quinoline:

I. 0, 4, 4, 5, 5, 5, 5, 2, 3, 3, 1, 3, 2, 3, 1, 1, 1, 0, 2, 1, 2, 1, 1, 2, 0, 0, 1, 0, 1, 1.
(60 atm. in 7½ hrs. = 8 atm./hr.)

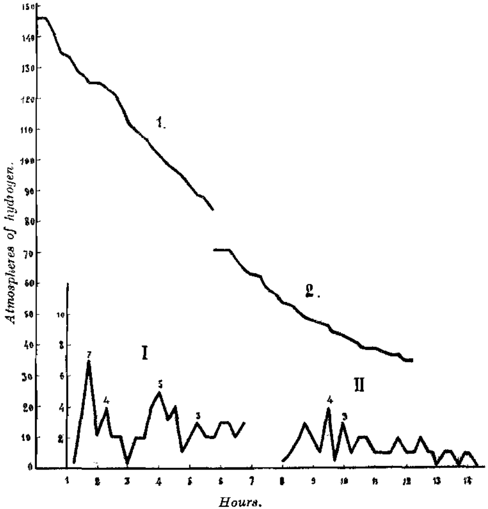
II. 2, 0, 1, 0, 1, 0, 0, 1, 0, 1, 1, 0, 0, 1, 0, 1, 0, 0, 1, 0, 0.
(10 atm. in 5¼ hrs. = 1·9 atm./hr.)

93% of tetrahydroquinoline was produced.

For 20% osmium-asbestos at 300° the following ranges were obtained (see Fig. 2):

FIG. 2.

Quinoline. 20% Os *on asbestos;* 300°.



I. ... 0, 4, 7, 2, 4, 2, 2, 0, 2, 2, 4, 5, 3, 4, 1, 2, 3, 2, 2, 3, 3, 2, 3.
(62 atm. in 5½ hrs. = 10·8 atm./hr.)

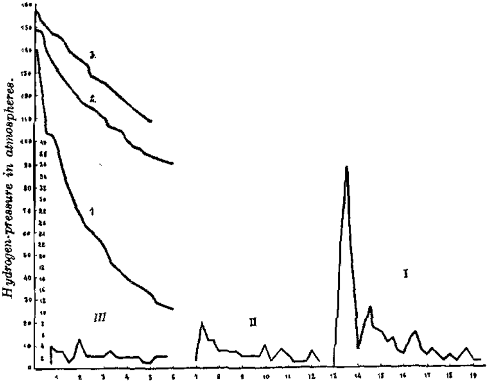
II. ... 0, 1, 2, 3, 2, 1, 4, 1, 3, 1, 2, 2, 1, 1, 1, 2, 1, 1, 2, 1, 0, 1, 1, 0, 1, 0.
(35 atm. in 6¼ hrs. = 5·6 atm./hr.)

If only 1% of ceric oxide be added to the foregoing 20% osmium-

asbestos, considerable initial acceleration and increased intensity result (see Fig. 3):

FIG. 3.

Quinoline. Osmium 20 % + CeO_2 1 % *on asbestos;* 320°.



I. ... 35, 3, 6, 1, 1, 7, 6, 4, 5, 3, 2, 5, 6, 3, 2, 3, 2, 1, 2, 1, 2, 3, 1, 1.
(105 atm. in 6 hrs. = 17·5 atm./hr.)

II. ... 1, 8, 5, 5, 3, 3, 3, 3, 2, 2, 2, 2, 4, 1, 2, 3, 2, 1, 2, 1, 1, 1, 3, 1.
(61 atm. in 6 hrs. = 10 atm./hr.)

III. ... 4, 3, 3, 1, 2, 5, 2, 2, 2, 2, 3, 2, 2, 2, 2, 2, 2, 2, 1, 1, 2, 2, 2.
(51 atm. in 5¾ hrs. = 9 atm./hr.)

Products of reaction:

Temp. range.	165—200°.	200—240°.	240—250°.	260° and above.
NH_3%	66·7	17·0	3·3	13·2

In order to emphasise the significance of the addition of ceric oxide, the two foregoing experiments are compared in the following table:

	20% Os–Asbestos.	20% Os–Asbestos + 1% CeO_2.
Maximum in the course of 15 mins. ...	7 atm.	35 atm.
Maximum in the course of 60 mins. ...	15 ,,	45 ,,
Average quantity of H_2 absorbed per hour (I)	10·8 ,,	17·5 ,,
Average quantity of H_2 absorbed per hour (II)	5·6 ,,	10 ,,
Average quantity of H_2 absorbed per hour (III)	—	9 ,,

Owing to the presence of ceric oxide, the activity of osmium undergoes a comparatively rapid restoration, and in each of the three ranges there is a total absence of zero values. In each case the initial activity is immediately followed by a temporary fatigue, and periods of activity and depression then alternate. This example clearly demonstrates the discontinuity of the hydrogenation. Oxygen doubtless participates in the reactivation, both in the layer of osmium tetroxide and in the ceric oxide which serves as a promoter or subsidiary activating agent.

Althongh ceric oxide, when distributed over asbestos to the extent of 20%, will facilitate the hydrogenation of quinoline, giving as much as 88% of tetrahydroquinoline, yet, in the absence of any catalysing metal, it is incapable of hydrogenating pyridine, naphthalene, or benzene; similarly, it is unable to effect further reduction of tetrahydroquinoline and hexahydroquinoline, whereas this is easily effected on the addition of osmium or nickel. Thus, although osmium and cerium jointly produce intense hydrogenation, neither of these alone is capable of giving such an effect. Similar results are obtained for the formation of low-boiling products (below 200°) when a combination of 20% CeO_2 + 1% Os is used instead of 20% Os + 1% CeO_2 (compare p. 447).

The following significant data were obtained on hydrogenating benzene or pyridine in the presence of 20% osmium–asbestos (1) alone, and (2) with the addition of ceria:

(1) *Benzene*; Osmium, 20% on asbestos; 250°.

I. 0, 0, 2, 8, 6, 5, 4, 4, 4, 5, 3, 3, 4, 1, 4, 4, 4, 3, 4.
II. 0, 1, 1, 2, 2, 3, 2, 2, 2, 1, 4, 4, 2, 6, 1, 1, 1, 2, 1, 1, 0, 1, 0, 0, 0, 0, 1, 1, 0, 0, 0.
III. 0, 0, 5, 7, 6, 5, 5, 4, 5, 3, 2, 5, 2.
IV. 0, 0, 0, 2, 1, 1, 1, 0, 1, 1, 1, 1, 1, 1, 2. 1, 0, 1, 0, 0, 0, 0, 1, 1, 0, 0, 1, 0, 0, 0, 0.

Pyridine; Osmium, 20% on asbestos; 250°.

I. 0, 5, 19, 1, 1, 1, 3, 0, 1, 3, 2, 3, 2, 3, 2, 2, 4, 4, 3, 6, 1, 2, 4, 2, 2, 3, 2, 3, 1, 3, 2, 2, 2, 1, 1, 4, 2, 2.
II. 0, 2, 1, 2, 1, 2, 10, 3, 0, 1, 2, 1, 1, 1, 0, 1, 1, 1, 1, 0, 1, 0, 1, 0, 1, 1, 1, 0.

(2) Pyridine; 20% Os + 1% CeO_2 on asbestos; 250°.

I. 0, 0, 0, 0, 2, 2, 2, 2, 2, 1, 1, 1, 1, 1, 1, 1, 2, 2, 1, 0, 1, 2, 2, 2, 1, 1, 1, 1.
II. 0, 1, 1, 1, 1, 1, 1, 2, 1, 1, 2, 2.
III. 0, 0, 1, 0, 2, 1, 1, 0, 1, 1, 1, 1, 1, 2, 1, 1, 2, 0, 1, 1, 1, 0, 2, 2, 1, 0, 1, 2, 1, 0, 1.

(1) Comparing the hydrogen absorption during successive intervals of 15 mins., we see that benzene is not so readily hydrogenated as pyridine, the maximum in the first case being 8 atm., and in the second 19 atm.; however, in the course of the first run ($4\frac{3}{4}$-hours) in each case an almost equal number of atmospheres is absorbed per hour, *viz.*, 14 atm. in the case of benzene, and 12·5 in that of pyridine. The sharp rise of the curve up to 19 atm. with pyridine causes succeeding values to be lower (1 and 2 atm.),

whereas with benzene, the initial maximum being lower (8 atm.), the subsequent values are somewhat higher (4 atm.). Further, the extinction of the catalyst's activity takes place much more rapidly in the case of pyridine than in that of benzene.

(2) The addition to 20% osmium–asbestos of 1% of ceric oxide is followed by marked lowering of the rate of hydrogenation of pyridine, whereas in the case of quinoline a pronounced increase in the rate was noted (p. 444). One and the same catalytic system when applied to different compounds may thus display entirely opposite effects. Pyridine and benzene nuclei, when taken as forming part of the quinoline complex, apparently are endowed with other properties than when taken separately.

The foregoing method of investigating catalytic systems not only affords the possibility of estimating the catalytic power of a given "symbiosis" of catalytically acting substances, but also permits a closer study of the characteristics of various kinds of bonds in cyclic formations, whereby we may establish a relationship between the speeds of hydrogenation and the properties of cyclic bonds.

Thus, support is afforded to the assumption that the activity of the catalyst depends upon some sort of association with the substance undergoing hydrogenation. The extinction of the catalyst may depend, *inter alia*, upon lack of purity and homogeneity of the matter subjected to hydrogenation, *i.e.*, upon the presence therein of impurities or of products of hydrogenation which are inimical to the catalyst.

A careful examination of the curves obtained from many hydrogenations of quinoline in the presence of osmium–asbestos containing 1% of ceria reveals the same general tendency in spite of differences in degree: the sharp rise within the first 15 mins. characteristic of osmium and greatly enhanced by the presence of cerium, seems to denote a more or less noticeable concentration of the activity of the catalyst within this initial period. The catalyst behaves as if it were supplied with a definite initial charge of activity, which is being expended either *en bloc* during the first moments of action, or by small portions distributed throughout a number of intervals. This initial charge, after being more or less rapidly consumed, is partially restored within a short space of time, then expended anew and once more restored. The phases of accumulation are characterised by low or even zero absorption, being, as a rule, the longer the greater the previous manifestation of the catalyst's activity, and being considerably shortened in the presence of reactivating agents (*e.g.*, of ceric oxide).

It may sometimes happen, owing to causes not yet understood, that the catalyst selected gives signs of fatigue from the very

beginning of the process, being endowed with a low initial charge. There are even cases in which the charge is originally so low as to require a certain period of induction (or of accumulation), this condition being expressed by zero values throughout a whole range of 15-min. intervals.

The following results were obtained for the hydrogenation of quinoline in the presence of 20% CeO_2 + 1% Os on asbestos at 320°:

I. 3, 2, 3, 2, 6, 4, 5, 6, 5, 5, 5, 4, 5, 5, 4, 1, 4, 2, 4, 2, 2, 2, 2, 3, 2, 2, 2, 3.
II. 4, 2, 4, 2, 2, 2, 1, 3, 2, 1, 1, 3, 0, 1, 1, 1, 2, 1, 0, 1, 1, 1, 1, 0, 0, 0, 1.
III. 0, 10, 5, 6, 8, 4, 5, 3, 5, 4.
IV. 1, 4, 2, 2, 1, 3, 2 . . . 2, 0, 3, 1, 0, 1, 2, 2, 1, 0, 1, 1, 1, 1.

The initial 1-hour rate of the second period (12 atm.) is higher than that in the first period (10 atm.); also, in the third phase we have a 15-min. maximum of 10 atm., and 1-hour values of 21 and 20 atm. Thus, the deficiency in the initial increase (in the first 15 min.) is, as it were, compensated by a prolonged duration of activity, and by a more uniform expenditure of the catalytic force, which, in conjunction with a concurrent reactivation, gives the *impression of a certain catalytic equilibrium.*

These investigations give convincing evidence of the discontinuous character of the activity of the catalyst, which is most clearly exhibited when the easily oxidisable osmium is used in presence of ceric oxide as a promoter. Oscillations of activity are evidently closely allied with co-operation of oxygen, which regenerates the catalyst; the latter, during the process of hydrogenation, experiences a fatigue which is inherent in the nature of the catalytic process. Poisoning and complete exhaustion of the catalyst are to be considered as a mere summing up of natural moments of weariness—their accumulation in amounts high enough to exclude the possibility of automatic regeneration. But how shall we represent the oscillatory character of the catalytic activity? New light is being shed on this matter by the work of Bredig and Weinmayr (*Z. physikal. Chem.*, 1903, **42**, 600) on periodic contact catalysis, as well as by the investigations of Hedges and Myers (J., 1924, **125**, 604, 1282; 1925, **127**, 445, 1513) on the periodic character of the dissolution of metals *in acids and alkalis.* In the first case, we have to deal with *evolution* of oxygen, and in the second with that of hydrogen. In hydrogenating cyclic compounds in presence of osmium and ceric oxide, we meet for the first time with a case of periodicity in the absorption of gas.

Moreover, the phenomena now described present many points of difference from those observed by Ostwald, Bredig, Hedges, and others, for the latter occur at comparatively low temperatures (down to 35°), under atmospheric pressure, and in aqueous media.

On the other hand, those now described occur at higher temperatures, under high pressures, and in absence of water. In each case, however, there are periods of induction, rises and falls, stages of activity and passivity, and, lastly, exhaustion of the catalyst's power due, not only to the reagents being consumed, but also to degeneration of its efficiency.

The alteration in the appearance of the catalysing metal, which has been noted by Bredig and by Hedges, is in our case beyond the possibility of observation; nevertheless, the part played by oxygen, in forming suboxides, oxides, and peroxides, especially in the system osmium + ceric oxide, should be beyond doubt. The views of Hedges as to the formation of an amorphous, gas-free, highly occluding crust of metal on heating in a vacuum do not exclude the significance of the alternate ripening and disappearance of oxide laminæ, the more so as this phenomenon closely corresponds to the rhythmic pulsations in the evolution of gases and in electric potential. The thermal preparation of the catalyst, combined with the addition of the second metallic component (promoter), gives identical results as to periodicity in the interaction of the reagents. In our cases, the thermal preparation of the catalyst assumes a permanent character owing to the fact that the reaction is being effected only within the limits of a definite optimal range of temperature. The formation of the oxide lamina is ensured both by the presence of ceric oxide and by the easy oxidisability of osmium, whereas the disappearance of the lamina (regeneration of the occluding metal) is due to the presence of hydrogen which is capable not only of hydrogenating but also of exerting a reducing influence.

STATE INSTITUTE OF APPLIED CHEMISTRY,
LENINGRAD. [*Received, August 2nd*, 1927.]

LXI.—*The Laws of Aromatic Substitution. Part VI. A Quantitative Method for the Rapid Determination of Isomeric Nitro-derivatives of Laterally Substituted Toluenes.*

By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES.

INVESTIGATIONS on the influence of substituted methyl groups on the positions taken by nitro-groups entering the nucleus are generally faced with two problems: uniform oxidation of all the isomerides to the corresponding acids, and accurate determination of the relative proportion of *o*- and *p*-nitrobenzoic acids on the one hand and *m*-nitrobenzoic acid on the other.

I. *Oxidation.*—(A) *Permanganate.* As long ago as 1877, Michael and Norton (*Ber.*, **10**, 580) stated that *p*-nitrotoluene gives a good yield of *p*-nitrobenzoic acid when boiled with a solution of 1 part of permanganate in 40 parts of water. Actual figures, or the comparative yields obtained on oxidation of isomeric nitrotoluenes, were, however, not given. In Part V of this series (J., 1926, 1562) we showed that, when an even weaker solution (for instance 1 : 60) was employed, the acids were obtained in yields of about 80% of the theoretical and, what is more important, that the percentages were practically identical for all three nitro-isomerides. These results have since been utilised by Ingold and his co-workers.

We have applied the method to a large number of compounds (see chiefly Parts VIII, IX, and X of this series) without a single failure. In two cases (phenylnitromethane and ethyl phenylbromomalonate), the dilution being 1 : 60, *gradual* addition of the permanganate produced a less pure, yellow acid mixture, whereas the usual colourless product was obtained when the permanganate had been added all at once. In some experiments involving specially mobile substituents, certain modifications were introduced (see following paper). The method is simplified by destroying the residual permanganate with sulphur dioxide, which simultaneously dissolves the manganese dioxide, filtration being thus obviated.

(B) *Dilute nitric acid.* Nitric acid (*d* 1·10—1·15) was employed by Baker and Ingold (J., 1926, 2468) for the oxidation of nitration products. This agent is not of such general applicability as permanganate (see following paper), but where it can be used our tests prove it to be equally satisfactory. The resistance to destructive oxidation is again almost identical for the isomeric acids, and is much the same as with permanganate (see experimental part). Baker and Ingold's statement that benzoic acid is not nitrated under these conditions is essentially correct; our more delicate method, however, has enabled us to show that nitration under Baker and Ingold's average conditions takes place to the extent of about 1%.

II. *Determination of the Proportion of the Isomerides.*—Francis and Hill (*J. Amer. Chem. Soc.*, 1924, **46**, 2498) devised a method for estimating the percentages of *o*- + *p*- and of *m*-nitrobenzoic acids based on the consumption of two atoms of bromine by the former acids and of three atoms of bromine by the latter acid after reduction to amino-acids. These authors also directed attention to a source of error, due to partial replacement of carboxyl by bromine, resulting in an increased consumption of bromine. The method, therefore, could give trustworthy results only if the degree of such replacement were always the same for a given mode of operating. But since the three amino-acids and their partly brominated deriv-

atives cannot all be assumed to take up bromine at the same rate, it seems clear that the extent to which carboxyl is eliminated from the *o*- and *p*-acids must vary, even under otherwise similar conditions, with the initial composition of the mixture—and, whenever an intermediate solid phase is formed, also with unavoidable physical differences. It is not surprising, therefore, that Ingold and his co-workers appear to have abandoned this method in favour of more laborious processes, including the removal of benzoic acid by sublimation and the old method of barium-salt precipitation and fractional recrystallisation, which we ourselves had utilised in Part V of this series. These tedious separations, however (and this applies to the solubility method also), do not give even approximately accurate results when certain substances—such as the bromo- and nitrobromo-acids encountered in Part VII—are present, and therefore the discovery of a better method became imperative. A suggestion made by Mr. W. B. Saville, that *m*-bromobenzoic and benzoic acids might be separated from nitro-acids after reduction of the latter with titanous chloride (which would render them soluble in dilute acid), led us to consider the feasibility of separating the amino-acids from one another by introducing a difference in their behaviour towards acids or alkalis. No difficulty was experienced in converting *o*- and *p*-aminobenzoic acids at room temperature * *quantitatively* into tribromoaniline by prolonged exposure to bromine in dilute hydrochloric acid, and separation from the tribromo-*m*-aminobenzoic acid simultaneously formed from *m*-aminobenzoic acid was then easily effected by alkaline reagents. *Whereas, therefore, by Francis and Hill's method* three *bromine atoms are introduced into one of the aminobenzoic acids, and* two *(plus an indeterminate fraction) into the other two, and the bromine consumption constitutes the measure, by our method all three acids take up* exactly three *atoms of bromine, and the actual weights of the two compounds, formed with a high degree of purity, are the measure.*

EXPERIMENTAL.

I. *Oxidation.*—(A) *Resistance of acids to permanganate.* (a) 0·50 G. of benzoic acid was boiled for 3 hours with 1 g. of potassium per-

* Francis and Hill (*loc. cit.*, p. 2500) observed quantitative conversion of *o*- and *p*-aminobenzoic acids into tribromoaniline only at temperatures above 40°, and at the ordinary temperature only in the presence of sufficient alcohol to prevent precipitation of intermediate compounds. A *gravimetric* method was suggested by these authors only for hydroxybenzoic and aminosulphonic acids. It differs in principle from our method and, moreover, could not be applied to our problems, since it depends, not on selective salt formation as in our case, but on the—comparatively rare—occurrence of complete selective solubility in the absence of salt formation.

manganate in 60 c.c. of water and 2·5 c.c. of 10% aqueous potassium hydroxide. 0·447 G. (89·4%) of benzoic acid was recovered.

(b) 0·50 G. of *m*-bromobenzoic acid was treated as described above, but with only 1·6 c.c. of potash solution. Recovery = 0·452 g. = 90·4%.

(c) 0·25 G. of each of the three nitrobenzoic acids were mixed and boiled for 3 hours with 1·5 g. of permanganate in 90 c.c. of water and 2·5 c.c. of 10% aqueous potassium hydroxide. Recovery = 0·602 g. = 80·3%.

The yield of nitrobenzoic acids obtained on oxidation of a mixture of laterally substituted nitrotoluenes is, as a rule, higher than the recoveries recorded above, because the permanganate solution becomes more and more exhausted as the concentration of the acids formed increases.

(B) *Resistance of acids to nitric acid* (*d* 1·1244—1·1253). (a) 1 G. of benzoic acid was boiled for 6 hours with 50 c.c. of nitric acid (*d* 1·1244). The recovered acids, on reduction and bromination as described under II, gave 0·904 g. of benzoic acid, 0·003 g. of tribromoaniline, and 0·031 g. of tribromo-*m*-aminobenzoic acid (= 0·014 g. of *m*-nitrobenzoic acid).

(b) 0·25 G. of each of the three nitrobenzoic acids and 0·25 g. of benzoic acid were boiled together for 6 hours with 50 c.c. of nitric acid (*d* 1·1253). The recovered acids yielded 0·237 g. of benzoic acid (94·8% recovery), 0·814 g. of tribromoaniline (= 0·412 g. of *o*- + *p*-nitro-acids: 82·4% recovery), and 0·462 g. of tribromo-*m*-aminobenzoic acid (= 0·206 g. of *m*-nitro-acid: 82·4% recovery). Baker and Ingold (*loc. cit.*) employed acid of *d* 1·10—1·15 and boiled the solutions for 2—10 hours.

II. *Determination of the Proportion of the Isomerides.*—The acids are boiled with sufficient 10% hydrochloric acid to dissolve them, and aqueous titanous chloride (Knecht and Hibbert's method; also used by Francis and Hill) is then added until, after 10 minutes' boiling, the solution is still coloured. After cooling to room temperature, any non-amino-acids present (benzoic, bromobenzoic, etc.) are removed by ether. (Ether is the most suitable solvent for benzoic acid, because loss by volatility is minimised; for other mixtures other solvents, such as chloroform, may be found preferable.) After air has been bubbled through the aqueous liquid to remove all the ether, bromine water is added in not too large excess, and the mixture is left for 24 hours at room temperature, initially with occasional shaking. Any solid is then filtered off, washed with water, then several times with potassium bicarbonate solution and again with water, and dried to constant weight at 80° (at 100° it slowly sublimes). This is 2 : 4 : 6-tribromoaniline. The acid mother-liquor of this precipitate is freed from bromine by a current

of air and twice extracted with ether, and the extracts are shaken with an excess of bicarbonate solution, dried, and evaporated, yielding a further quantity of tribromoaniline. The several bicarbonate extracts are united and acidified, and 2 : 4 : 6-tribromo-3-aminobenzoic acid is then obtained, partly as a precipitate and partly by extraction of the filtrate therefrom with ether.

A special test showed that no appreciable portion of the aminobenzoic acids is withdrawn from the acid solution by the ether: 1 g. of a mixture of equal parts of the three nitrobenzoic acids was reduced and then twice extracted with ether as usual; the extracts left only 0·004 g. (oil) on evaporation.

When, in addition to aminobenzoic and non-aminobenzoic acids, a "negatively" substituted aminobenzoic acid, the salt of which with an inorganic acid would be largely dissociated in dilute solution, is present, its amount can be determined by a slight variation of the above procedure. If, for instance, bromoamino-acids (compare Part VII) are present, the solution of the initial mixture of reduced acids is repeatedly shaken with ether, until not more than 0·001 g. per g. of the original mixture of unreduced acids is extracted (in Part VII, 4 extractions were necessary in the case of 24-hour nitrations, and 8 for 10-day nitrations). The united ethereal extracts are washed with 15—20 c.c. of 10% hydrochloric acid, and this acid extract is shaken once with ether and then added to the main aqueous portion before bromination. The combined ethereal extracts are dried and, after addition of 10 c.c. of glacial acetic acid, distilled until no ether is left; the residual solution, after addition of 2 c.c. of bromine per g. of the original mixture, is kept for 24 hours, then diluted with water, and freed from bromine by a current of air. Any precipitate produced by the dilution is filtered off, before the bromine is removed, and is washed with bicarbonate solution: this leaves undissolved a portion of the tribromoaniline produced from the bromonitro-acid. The remainder of such tribromoaniline is obtained by adding an excess of bicarbonate to the filtrate from the above precipitate, shaking the solution with ether, and drying and evaporating the ethereal extract. All the alkaline liquors are now united, acidified, and shaken with ether, whereby the non-amino-acids (*e.g.*, benzoic and bromobenzoic acids) are obtained.

III. *Results with Synthetic Mixtures.*—

	I.			II.			III.		
Acids.	% Taken.		% Found.	% Taken.		% Found.	% Taken.		% Found.
m-Bromobenzoic	10·02	50·12	49·65	0		0	0		0
Benzoic	40·10			34·30		34·62	31·26		32·01
o-Nitrobenzoic ...	0	40·15	40·75	19·19	40·05	40·28	15·18	34·48	34·51
p-Nitrobenzoic ...	40·15			20·86			19·80		
m-Nitrobenzoic ...	9·73		9·60	25·65		25·10	34·26		33·48
	100·00		100·00	100·00		100·00	100·00		100·00

The figures under "% Found" are percentages of the total yield.

In II and III, the results were obtained without prior disclosure of the compositions of the mixtures.

A sample of purchased " pure " *m*-nitrobenzoic acid (m. p. 138—139°, instead of 141°) gave, when ground and heated for 4½ hours at 100° before weighing, reduction, and bromination, 2·227 g. of tribromoaminobenzoic acid and 0·009 g. of tribromoaniline per g. of material, equivalent to 99·44% of *m*-nitrobenzoic and 0·45% of *o*- and *p*-nitrobenzoic acids.

IV. *Calculation of Molecular Percentages.*—In the above tests, special care was taken to avoid volatilisation of benzoic acid. But quicker working is possible if, in the absence of other volatile materials, the weight of benzoic acid is calculated by difference. In Part VII, for instance, from the weights of the tribromoaniline produced from nitrobenzoic acids, of the tribromoaniline from bromonitro-acids, and of the tribromoaminobenzoic acid, the weights of *p*-(*o*-)nitrobenzoic, bromonitrobenzoic and *m*-nitrobenzoic acids, respectively, in the original mixture were calculated. From a bromine analysis of the original mixture the corresponding weight of bromobenzoic acid was calculated, from which, by subtraction of the bromonitrobenzoic acid—also calculated as bromobenzoic acid—the weight of un-nitrated bromo-acid was obtained. The difference between the weight of the original acid mixture and the sum of the calculated weights of all these fractions gave the weight of benzoic acid. From these figures the molecular percentages were calculated in the usual way.

We desire to express our indebtedness to the Advisory Council of the Department of Scientific and Industrial Research for a grant to one of us (E. L. H.) which has enabled him to collaborate in this work; also to Sir W. H. Bragg and the Royal Institution, who have placed at our disposal the facilities of the Davy Faraday Laboratory, where the investigation was carried out.

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LXII.—*The Laws of Aromatic Substitution. Part VII. The Constitution and Substitution of Phenylnitromethane and Some of its Derivatives.*

By Bernhard Flürscheim and Eric Leighton Holmes.

Baker and Ingold (J., 1926, 2462) nitrated phenylbromocyanonitromethane and obtained results differing materially from those which one of us had recorded (*J. pr. Chem.*, 1902, **66**, 321). They

thereupon asserted that those early experiments had been carried out incorrectly. We have now completed an exhaustive examination of the reaction, with the following results :

1. Contrary to the statement of Baker and Ingold, the experimental observations published by one of us (*loc. cit.*) have been found correct throughout. Phenylbromocyanonitromethane yields, on *brief* treatment with nitric acid (*d* 1·480) and subsequent oxidation by the usual methods, *practically only benzoic and p-nitrobenzoic* acids (see Experimental, section III, 8, d; p. 480), exactly as stated in 1902.

2. This *p*-nitrobenzoic acid—amounting usually to 34—38% of the weight of the total acids—arises essentially from the migration of the nitro-group during the oxidation. The occurrence of this migration, which can be prevented by prior treatment with alkali (see section IIIB; p. 463), has been quantitatively proved.

3. *m*-Nitration can occur under various conditions, as stated by Baker and Ingold, but it does not take place appreciably under the *conditions, nor even approximately in the proportion, recorded* by these authors (see sections IA and IV; pp. 456, 465).

4. The complex changes occurring on *prolonged* exposure of phenylbromocyanonitromethane to nitric acid (*d* 1·480) have been quantitatively elucidated. The main change—the migration of bromine into the *m*-position (see sections IB and IV; pp. 457, 466)—occurs to the extent of 54% in 10 days, and the rate of formation of the *m*-bromophenyl compound is independent of the concentration.

5. The *correlated behaviour of phenylcyanoisonitromethane,* benzoyl cyanide and *m*-bromobenzoic acid on nitration has also been quantitatively ascertained (see sections IB and IV; pp. 461, 466).

6. The following (primary) nitro-derivatives are formed *directly* by nitration of the compounds named :

Phenylbromocyanonitromethane, $C_6H_5\cdot\overset{\frown O \frown}{C(CN)\text{-}N}\cdot OBr$ (in nitric acid, *d* 1·52) : 92—93% of *m*-nitrophenylbromocyanonitromethane and 8—7% of the corresponding *p*(and *o*)-nitro-compound.

Phenylcyanoisonitromethane, $C_6H_5\cdot C(CN){:}NO\cdot OH$ (in nitric acid, *d* 1·480) : more than 99% of *p*-nitrophenylcyanoisonitromethane.

Benzoyl cyanide, $C_6H_5\cdot CO\cdot CN$ (in nitric acid, *d* 1·52) : 87·6% of *m*-nitrobenzoyl cyanide and 12·4% of *o*- and *p*-nitrobenzoyl cyanides.

m-Bromobenzoic acid (in nitric acid, *d* 1·480): 96% of *o*- and *p*-nitro-*m*-bromobenzoic acids and 4% of *m'*-nitro-*m*-bromobenzoic acid.

7. The migration of the nitro-group during the oxidation of phenylcyanonitromethane has been discovered and quantitatively examined (see section IIIB; p. 464). It occurs to the extent of 14 mol.%.

8. The decomposition of phenylbromocyanonitromethane and its *m*-nitro-derivative by heat alone, by hot dilute nitric acid, and by concentrated sulphuric acid (see sections IIIA, IIIB, and II; pp. 462, 464) and also the rearrangement of phenylbromocyanonitromethane in ethereal solution (see Experimental, section III, 3; p. 476) have been quantitatively studied. For example, the decomposition of phenylbromocyanonitromethane by heat yields 92 mol.% of benzoyl cyanide and 8 mol.% of *p*-nitrobenzoyl cyanide.

9. Phenylbromocyanonitromethane has been found to be a hypobromite, with an oxygen bridge (see 6), in accordance with Willstätter and Hottenroth's formula for tertiary bromonitro-compounds—a formula which is now co-ordinated with other observations by certain suggestions concerning tautomerism (see section V; p. 467). Hypobromite reactions of phenylbromocyanonitromethane and its newly discovered *m*-nitro-derivative have been quantitatively examined. Phenylbromomalonic ester—a true bromide—does not display such reactions at the ordinary temperature; at 95°, however, there is equilibrium between the hypobromite form and the bromide form, the latter greatly preponderating.

In the nitration performed by one of us (*loc. cit.*), nitric acid of *d* 1·480 * (8 parts, in a freezing mixture) was used. Baker and Ingold, who employed nitric acid of *d* 1·49 (8 parts, in a freezing mixture) obtained acids which, according to their analysis, were almost free from benzoic acid and contained an average of about 52% of *m*-nitrobenzoic acid. Our present investigations prove that no *m*-nitration is produced by acid of *d* 1·480 and very little by acid of *d* 1·490. When, however, the strength or relative amount of the acid, or the temperature or time of nitration, is increased, phenylbromocyanonitromethane may be nitrated appreciably or even completely, the proportion of the *m*-isomeride formed in the latter

* The work was done at Heidelberg in 1902 with "rauchende Salpetersäure." Reference to Blücher's "Auskunftsbuch," 1903, shows that "gelbe rauchende Salpetersäure" (usually called "rauchende" merely) was acid of *d* 1·480.

case being, not Baker and Ingold's 52%, but 92—93%. Whenever the nitration has not been carried to completion, the unchanged phenylbromocyanonitromethane partly undergoes re-arrangement during oxidation under the usual conditions and thus the percentage of the *p*-isomeride in the nitrobenzoic acids is increased, but, contrary to Baker and Ingold's statement, *p*-nitrobenzoic acid is in this case always accompanied by benzoic acid in preponderating amount.

The behaviour of phenylbromocyanonitromethane as a hypobromite enabled us to follow the course of the reactions occurring during nitration and the changes in the side chain and in the nucleus. The procedure is summarised as follows: A sample of the nitration product was treated with aqueous potassium iodide and the liberated iodine was titrated. What did not go into the potassium iodide solution (*i.e.*, products with *partly* altered side chain) was oxidised to the acids ($R·C_6H_4·CO_2H$) and the molecular composition of these was determined. The difference between this composition and the molecular composition of the acids obtained by oxidation of the initial nitration product (exclusive of acids formed during the *nitration*; see *below*) *gave the molecular composition* (*which could* not be determined directly) of the acids due to oxidation of the portion of the nitration product which was soluble in potassium iodide solution and therefore contained an unaltered hypobromite side chain. The acids formed during the nitration itself were separated initially by their solubility in potassium bicarbonate solution, and their molecular composition was determined directly. Migration during oxidation was prevented by prior treatment with alkali.

I. *Reactions of Phenylbromocyanonitromethane in Nitric Acid of Various Strengths and in Various Proportions.*

A. *In Kahlbaum's Nitric Acid* (d 1·52).—The nitromethane undergoes *m-nitration* (92—93%) and *p(and o ?)-nitration* (8—7%).

A large proportion of the *m*-nitrophenylbromocyanonitromethane was isolated in the pure state and analysed. The position of the nitro-group was proved by transformation into *m*-nitrobenzoyl cyanide and *m*-nitrobenzoic acid. That phenylbromocyanonitromethane and its *m*-nitro-derivative contain side chains having the same hypobromite constitution was shown by their giving the same reactions (see section V; p. 468). The composition of the remainder of the nitration product was ascertained by determining the percentages of the isomeric acids obtained by oxidation. The absence of benzoic acid proved that nitration was complete.

B. *In Nitric Acid* ($d^{15°}$ 1·480).—

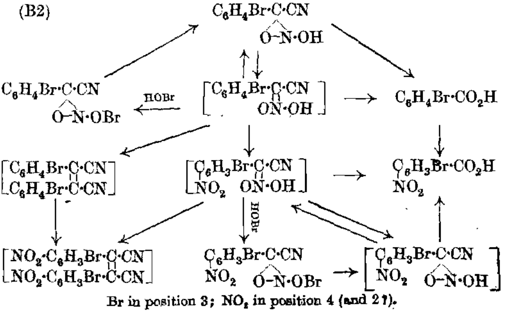
(B1) $C_6H_5\cdot\overset{\frown O \frown}{C(CN)\cdot N}\cdot OBr \longrightarrow m\text{-}C_6H_4Br\cdot\overset{\frown O \frown}{C(CN)\cdot N}\cdot OH.$

The transfer of bromine from the side chain to the *m*-position in the nucleus was quantitatively established by determining the bromine content of the acids obtained by oxidation, by isolating from these acids a large proportion of pure *m*-bromobenzoic acid, and by the fact that the portion of the nuclear bromo-compounds which had undergone nitration yielded, after oxidation, reduction, and bromination, nearly pure 2 : 4 : 6-tribromoaniline. That this transfer of bromine is an intramolecular migration—and not bromination of one molecule by another—follows from the observations that the rate of transfer is independent of concentration and is not affected by the addition of a substance containing a *m*-directing group. The latter fact was proved by adding to a solution of phenylbromocyanonitromethane in ether—in which also bromine was found to migrate—a large proportion of benzoyl cyanide. The migration of bromine, though slow, is the main change that occurs in nitric acid of *d* 1·480 : after 75 minutes, less than 3 mol.% had migrated; after 10 days, the nuclear bromine had increased to 54 mol.%.

The further changes undergone in nitric acid of *d* 1·480 by *m*-bromophenylcyanonitromethane (B2) and phenylbromocyanonitromethane (B3) are indicated in the following schemes.

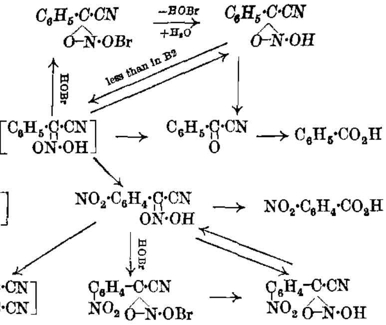
Names in square brackets donote products for the presence of which only indirect evidence was obtained.

(B2)



Br in position 3; NO_2 in position 4 (and 2?).

(B3)



NO_2 in position 4.

When *m*-nitration of phenylbromocyanonitromethane occurs, the *m*-nitro-derivative shows changes analogous to those given for the *p*-nitro-derivative in scheme B3.

The products represented in schemes B2 and B3 may be divided into three classes: (1) compounds with completely transformed side chain (benzoic acid and its nuclear-substituted derivatives); (2) compounds with intact side chain (phenylbromocyanonitromethane and its nuclear-substituted derivatives); and (3) compounds with partly transformed side chain (phenylcyanonitromethane, benzoyl cyanide, stilbene and their nuclear-substituted derivatives).

Transformation of the side chain to carboxyl does not—contrary to Baker and Ingold's indications—occur appreciably during the first few hours. At 13° and 15·5°, even after 6 days, only about 10% (by weight) of acids was formed. Compounds with a partly transformed side chain are, however, formed in a much higher proportion (*see section IV, p. 465, Table I, for exact figures*).

The nature of the partly transformed side chains. Benzoyl cyanide was detected by its unmistakable pungent odour.

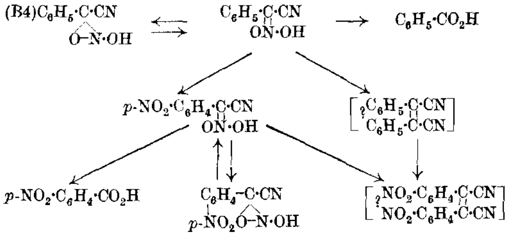
The presence of phenylcyanonitromethane and its nuclear derivatives was conclusively established by the following facts: in some of the earlier experiments, the portion of the nitration product insoluble in potassium iodide solution was oxidised without precautions to prevent migration, and yielded many times more than the true amount of *p*-nitrobenzoic acid. This unique reaction (compare section IIIB; p. 464) leaves no doubt as to the presence of phenylcyanonitromethane. The presence of its nuclear derivatives

follows from the proved presence of relatively large proportions of *m*-bromo-, *p*-nitro-, and 4-(2-)nitro-3-bromo-phenylbromocyanonitromethane among the compounds with an *unaltered* side chain after 6 days' nitration: the *m*-bromo- and 4-(2-)nitro-3-bromo-compounds can only arise from the lateral bromination of the initially produced corresponding compounds without side-chain bromine (compare formulæ B1; p. 457), and it is shown below that a similar explanation applies to the *p*-nitro-compound. Now we found that hypobromous acid reacts instantaneously with phenylcyano*iso*nitromethane to form phenylbromocyanonitromethane. Partial hydrolysis (see scheme B3; p. 458) of phenylbromocyanonitromethane to phenylcyanonitromethane in nitric acid of *d* 1·480 supplies hypobromous acid, which then combines with the *iso*-forms of phenylcyanonitromethane and of its nuclear derivatives.

Since the equilibrium between a nitro- and an *iso*nitro-form alters in favour of the latter with increasing "negative" substitution (Hantzsch), the proportion of *m*-nitrophenylcyanonitromethane finally present as hypobromite (*m*-nitrophenylbromocyanonitromethane) is found to be greater than for the un-nitrated compound. Similarly, for the *m*-bromo-derivative this proportion, after a 6 days' nitration, is found to be ½ to ⅔ as high as for the unsubstituted compound, notwithstanding that the latter was originally already present as hypobromite and the former was not. For the *p*-nitro-compound the final proportion of hypobromite is found to be higher than for the unsubstituted compound, although here again it cannot have been a hypobromite when first formed, as we shall now show.

Simple nitration of phenylbromocyanonitromethane (see A; p. 456) leads almost exclusively to the *m*-nitro-derivative. But in nitric acid of *d* 1·480 the *p*-nitro-compound predominates over the *m*-isomeride, at least when not more than 13 parts of acid are used. It follows that only a negligible portion of the *p*-compound can owe its production to nitration of phenylbromocyanonitromethane. Nor can the immediate hydrolytic product of phenylbromocyanonitromethane, *viz*., phenylcyanonitromethane, account for *p*-nitration, because, whereas the concentration of this hydrolytic product increases as the reaction proceeds, the rate of *p*-nitration decreases. When, however, phenylcyano*iso*nitromethane in the nascent state is nitrated, whether by nitric acid of *d* 1·480 or of *d* 1·52 (*e.g.*, by nitrating its sodium salt), *p*-nitration occurs almost exclusively; a portion of the *p*-nitrophenylcyano*iso*nitromethane is then transformed into *p*-nitrobenzoic acid and the remainder isomerises to the "true" nitromethane (see p. 469) (and possibly some *pp'*-dinitrostilbene is formed; see below). And this is what also happens during the nitration of phenylbromocyanonitro-

methane—*with the difference that the concentration of the iso*-compound is relatively very low, and that hypobromous acid is



present. The latter not only reacts with *p*-nitrophenylcyano*iso*-nitromethane to form *p*-nitrophenylbromocyanonitromethane (compare above), but also, as it accumulates through the progressive initial hydrolysis of phenylbromocyanonitromethane, practically stops further *p*-nitration as a result of its exceedingly rapid reaction with the un-nitrated *iso*-compound. *m*-Bromophenylcyanonitromethane is similarly nitrated in its—somewhat more favoured—*iso*-form.

The formation of the remainder of the compounds with a partly transformed side chain, *viz.*, stilbene and its nuclear-substituted derivatives (*see schemes* B2 *and* B3; *pp.* 457, 458), *though not* absolutely proved, is rendered probable by the following consider*ation :*

Wislicenus and Elvert (*Ber.*, 1908, **41**, 4126) found that *p*-bromophenylcyano*iso*nitromethane, by treatment with dilute sulphuric acid, yielded not only *p*-bromobenzoic acid but also *pp'*-dibromodicyanostilbene. (They also stated that concentrated mineral acids produce *p*-bromobenzoic acid, but apparently had not observed the characteristic blue colour reaction referred to below.) An indirect indication of the formation of stilbene derivatives was obtained in our case in the bromonitrophenyl series. These derivatives, after a 6 days' nitration, were found only or almost only amongst the acids and in the portion of the product insoluble in potassium iodide, the essential absence of the potassium iodide-soluble hypobromite, and therefore of the hydrolytic product in equilibrium therewith, thus being indicated. Moreover, the benzoyl cyanide of the series could hardly have survived, since we found that nitrobenzoyl cyanides are hydrolysed with extreme ease. Barring these normal constituents of a product insoluble in potassium iodide, there

remained only the corresponding stilbene as a probable main constituent.

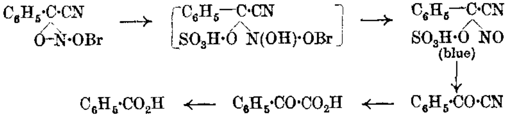
The mode of formation of the compounds with completely transformed side chains (acids). The above nitrations of *iso*-compounds show that, of each acid produced during the nitration of phenylbromocyanonitromethane, a portion must originate directly from the *corresponding isonitro*-compound. That the *p*-nitro-acid is not formed by some reaction of the *iso*nitro-group *prior* to nitration follows from the consideration that the intermediate products of such reaction, benzoylformic and benzoic acids and, as we have ascertained, benzoyl cyanide also, would be nitrated chiefly in the *m*-position in so far as they were nitrated at all, and that some of the *p*-nitro-product always retains its side chain with the original nitro-group. In the case of bromonitrobenzoic acid, a second portion is derived from the nitration of *m*-bromobenzoic acid, since we have found that this acid is slowly nitrated in 86% nitric acid. The remaining portions of each acid are formed from the corresponding "true" nitrocyano-compounds (in their bridge form). This follows from the fact that the nitration of phenylbromocyanonitromethane produces much more benzoic acid than *p*-nitrobenzoic acid; since we found that the reverse held when phenylcyano*iso*nitromethane was nitrated, the excess of benzoic acid beyond what is attributable to the *iso*-form must arise from the "true" nitro-compound. This is confirmed by the analogous—but much quicker—action of concentrated sulphuric acid (I, 7 and 8; p. 455) on the bridge in phenylbromocyanonitromethane; here the expected intermediate nitroso-derivative (which can also isomerise to the hydroxamic acid in the case of primary nitro-compounds) attains such a concentration that it can be detected by its intense blue colour (see formulæ, section II; p. 462).

The *kinetics* of the process, for a given temperature, expressed by the molecular percentage yields obtained with various times and concentrations (section IV; p. 466), agree with the above considerations. Only approximate kinetic calculations are, of course, possible in this complicated case, but the ratio, for instance, of *p*-nitrophenyl produced to the mean of the unsubstituted phenyl initially and finally present shows a definite increase with increasing relative volume of acid; obviously because the rate of nitration of the *iso*-nitro-compounds remains unaffected, whereas the competing recombination with hypobromous acid is retarded. At the same time the ratio of total *m*-bromination to average phenyl present remains constant (unimolecular change). The rate of decrease of side-chain bromine, as indicated by titrations with potassium iodide, after the first until the sixth day is much slower than the kinetics

of the bromine-migration would require; it is explained by the formation of *m*-bromophenylbromocyanonitromethane from the corresponding *iso*nitro-compound and hypobromous acid.

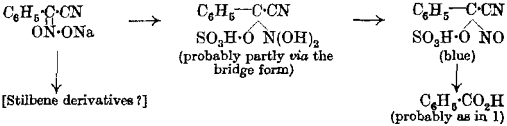
II. *Reactions in Concentrated Sulphuric Acid.*

(1) Phenylbromocyanonitromethane:



(2) *m*-Nitrophenylbromocyanonitromethane: Reactions analogous to those in (1).

(3) Phenylcyano*iso*nitromethane (sodium derivative):



The formation of a nitroso-compound in all three cases was indicated by the production of a blue colour. Benzoyl cyanide was identified in (1) by its odour. Benzoic acid was isolated in (1) and (3), and *m*-nitrophenylglyoxylic acid in (2). The latter compound (m. p. 144·5—145°) was also obtained from *m*-nitrobenzoyl cyanide by treatment with cold concentrated hydrochloric acid, and its nature confirmed by analysis and the thiophen test. The acid, m. p. 77—78° (after softening at 65°), described in Beilstein's "Organische Chemie" as *m*-nitrophenylglyoxylic acid must therefore, to say the *least*, have been very *impure*.

III. *Re-arrangements produced by Heating.*

A. Re-arrangements by Dry Heating.—(1) Phenylbromocyanonitromethane gives bromine, nitric oxide, benzoyl cyanide (92 mol.% found; more than 72 mol.% isolated) and *p*-nitrobenzoyl cyanide (8 mol.% found; 7·5 mol.% isolated).

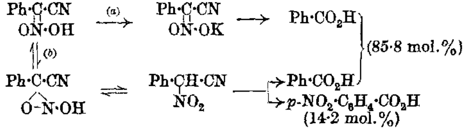
(2) *m*-Nitrophenylbromocyanonitromethane gives *m*-nitrobenzoyl cyanide (93·5 mol.% isolated) and a brominated mixture (8% of the weight of *m*-nitrophenylbromocyanonitromethane used).

When phenylbromocyanonitromethane was prepared for the first

time (by one of us, *loc. cit.*), its decomposition by heat, and two substances produced thereby, were described. One of these substances was later identified by Wislicenus and Schäfer (*Ber.*, 1908, **41**, 4169) as benzoyl cyanide. They isolated the other, still impure and not analysed, in a yield of 1·6 mol.%, and hydrolysed it to *p*-nitrobenzoic acid; they thought it "might possibly be *p*-nitrobenzoyl cyanide." We have now isolated it in a yield of 7·5 mol.% and proved it to be *p*-nitrobenzoyl cyanide by obtaining a constant melting point agreeing with Zimmermann's (*J. pr. Chem.*, 1902, **66**, 353) and by analysis. Since the total migration of NO_2, determined by oxidation, exceeded this 7·5 mol.% by only 0·5 mol.%, *o*-migration must be negligible.

m-Nitrobenzoyl cyanide, similarly obtained from *m*-nitrophenylbromocyanonitromethane, was identified by its properties, by analysis, and by hydrolysis to *m*-nitrobenzoic acid.

B. *Re-arrangements by Heating with an Oxidising Agent in Aqueous Solution.*—(a) *With permanganate.*

(1) 

(2) Ph·C·CN (ON·OK (or NH_4)) ⟶ Ph·CO_2H; ⟶ hydrolysis, then reactions as in 1*b* (mol.% of *p*-nitro-acid = 2·8 for NH_4-salt and 0·1 for K-salt).

(3) Ph·C·CN (O–N·OBr) ⟶ *p*-NO_2·C_6H_4·CO_2H (12·5 mol.%) + Ph·CO_2H (87·5 mol. %).
= 30% thermal decomposition, yielding 8 mol.% of *p*-nitro-compound (see III A1; p. 462), + 70% hydrolysis, yielding 14·2 mol.% of *p*-nitro-compound (see 1*b* above).

(4) Ph·C·CN (O–N·OBr) in presence of 0·93 times its weight of Ph·CO·CN, whereby reaction 1*a* (above) is retarded, but 1*b* is unaffected, ⟶ *p*-NO_2·C_6H_4·CO_2H (21·5 mol.%) + Ph·CO_2H (78·5 mol.%).

(b) *With nitric acid*, d 1·125.

(5) Ph·C·CN (O–N·OBr) ⟶ *p*-NO_2·C_6H_4·CO_2H (11—12 mol.%) + Ph·CO_2H (89—88 mol.%), which corresponds to about half hydrolysis (III B1, above) and half thermal decomposition (III A1; p. 462).

The scheme for III B1 (p. 463) is proved by the fact that hardly any migration occurs when the potassium salt of phenylcyano*iso*-nitromethane is oxidised (III B2). The *iso*nitro-group is stabilised in the order :NO·OK>:NO·ONH_4>:NO·OH, so that *p*-migration is observed *in the inverse order. In a substance containing the group* :NO·OK hardly any migration occurs, and in agreement with this we found that such a substance was only very slightly hydrolysed in aqueous solution. III B3 follows immediately, and III B5 approximately, from III A1 (p. 462) and III B1. An admixture of *an alkali-insoluble material, as in III B4, hinders the transformation* of phenylbromocyanonitromethane into the potassium salt and therefore favours *p*-migration. This explains why, when phenylbromocyanonitromethane in presence of the only partly alkali-insoluble products of its reaction with 86% nitric acid is heated with *permanganate (without first converting it into the potassium salt),* much more *p*-nitrobenzoic acid is found than in III B3. And when —as in the 1902 experiment of one of us—such heating is carried out after a nitration of brief duration, then, apart from traces of *m*-bromo- and (possibly) *o*-nitro-benzoic acid too small for detection by separation, only *p*-nitrobenzoic and benzoic acids can be found—exactly as one of us had recorded (*loc. cit.*).

Although this migration of a nitro-group during a permanganate oxidation appears to be unique, it is quite intelligible, since it occurs in the following phases: (1) (in the case of phenylbromocyanonitromethane) Hydrolysis to phenylcyanonitromethane, with participation of the aqueous permanganate solution. (2) Decomposition and re-arrangement of that portion of the phenylcyanonitromethane which does *not* go into solution as *iso*-ion. This decomposition and re-arrangement occur in the suspended oil *without* participation of the aqueous permanganate solution. (3) Oxidation of the products of re-arrangement and decomposition, with participation of the permanganate solution.

It should further be pointed out that in oxidation method A (see Experimental, p. 471), which produces re-arrangement, boiling is carried out with solutions of alkali of a somewhat higher concentration than in method C (p. 471), which precludes re-arrangement; only the *initial* heating to the boiling point is performed in the presence of alkali in the one case and in its absence in the other. It is therefore not possible to argue that the *p*-nitrobenzoic acid obtained by method A is derived from a *p*-nitro-derivative originally present and that this derivative, if treated as in method C, would be destroyed by the alkali. Quite apart from this, alkali has no such effect under our conditions, as is shown by the identical yields obtained in the oxidation of *p*-nitrobenzaldehyde with and without

alkali (Experimental, III 8 g; p. 481). Further, the facts that the oxidation of phenylcyanonitromethane and of its *iso*ammonium salt, each in the *absence* of added alkali, yields 14·2 mol.% of *p*-nitrobenzoic acid in the former case but only 2·8 mol.% in the latter, and that in the complete nitrations (acid of *d* 1·52) No. 17 (oxidation by method A) and No. 18 (oxidation by method C) identical yields of *p*-nitrobenzoic acid are obtained (no re-arrangement being possible in the absence of un-nitrated product), show conclusively that the portion of the *p*-nitrobenzoic acid produced by method A, but not produced by method C, can only arise by a re-arrangement.

IV. *Nuclear and Lateral (Side-chain) Changes during Nitration, expressed as Molecular Percentages.*

PBCN denotes phenylbromocyanonitromethane. The nitration numbers in Table I refer to the corresponding numbers in Table II.

Table I.

Lateral decomposition, mol.%.

Substance.	Products of nitration.	R = *m*-C_6H_4Br.	NO_2-*m*-C_6H_3Br.	*p*-(*o*-)$C_6H_4{\cdot}NO_2$.	*m*-$C_6H_4{\cdot}NO_2$.	C_6H_5.	Total.
1. PBCN (*nitration No. 10*):							
	$KHCO_3$-*soluble*: R·CO_2H	3·70	0·95	1·61	0·85	8·69	15·80
	KI-soluble: R·C·CN with ring O—N·OBr	10·79	0	2·32	3·39	23·38*	39·88
	Insoluble { R·C·CN with ring O—N·OH; R·CO·CN; [R·C(CN):]$_2$	14·09	8·25	0·90	0·08	20·40	44·32
2. PBCN (*nitration No. 11*):							
	$KHCO_3$-*soluble*: R·CO_2H	3·49	0·84	1·34	0·69	7·74	14·10
	KI-soluble: R·C·CN with ring O—N·OBr	8·72	1·07	1·99	3·48	23·42*	38·68
	Insoluble { R·C·CN with ring O—N·OH; R·CO·CN; [R·C(CN):]$_2$	10·81	8·24	1·15	0·79	17·23	47·22
3. C_6H_5·C(CN):NO·ONa (nitration No. 22):							
	$KHCO_3$-soluble: R·CO_2H	—	—	8·80	0·03	0·84	9·67
	$KHCO_3$-insoluble { R·C·CN with ring O—N·OH; R·CO·CN; [R·C(CN):]$_2$	—	—	80·93	4·05	5·35	90·33
4. C_6H_5·C(CN):NO·ONa (nitrations Nos. 23, 24):							
	$KHCO_3$-soluble: R·CO_2H	—	—	14·34	0·04	1·36	15·74
	KOH-soluble less $KHCO_3$-soluble { R·C·CN with ring O—N·OH	—	—	61·55	0·39	7·94	69·88
	Insoluble { R·CO·CN; [R·C(CN):]$_2$	—	—	4·23	0·09	10·06	14·38

* Original substance.

TABLE II.

Nitration No.	Parts of acid	and density.	Temp. and time.	Nuclear substitution, mol. %. Unsubstit.	m-Br.	Nitro-m-Br.	p(o-)-NO_2.	m-NO_2.
(1) PBCN.								
1, 2	52;	1·480	15°; 15 mins.	94·0	2·4		3·4	0·2
3, 4	13	,,	15°; 75 ,,	93·55	3·35		2·75	0·35
5, 6	52	,,	15°; 75 ,,	93·7	3·7		3·45	0·4
7	13	,,	13°; 24 hrs.	72·75	16·45	4·45	4·45	1·9
8	13	,,	room; 24 ,,	73·6	17·05	4·4	4·45*	0·5
9	52	,,	12·6°; 24 ,,	62·45	15·25	4·1	5·35	12·85
10	13	,,	13°; 6 days	52·5	28·85	8·95	4·8	4·9
11	13	,,	15·5°; 6 ,,	48·4	32·0	10·15	4·5	4·95
12	8	,,	room; 10 ,,	45·0	34·65	15·25	3·8	1·3
13	8	,,	,, ,,	41·05	53·05		3·8*	0·6
14	13	,,	,, ,,	37·4	34·9	19·25	5·1	3·35
15	13	,,	,, ,,	37·55	36·35	17·35	5·1*	3·65
16	52;	1·4805	12·6°; 24 hrs.	43·95	14·4	3·4	4·95	33·3
17	8;	1·52	15°; 15 mins.	0	0		7·15	92·85
18	8;	1·52	−10°; 1 hr., then room; 15 mins.	0	0		8·0	92·0
19	8;	1·500	15°; 2 hrs.	38·45			5·75	55·8
20	8;	1·490	Baker and Ingold's	96·7			1·65	1·65
21	8;	1·490	,, ,,	96·35			1·60	2·05
(2) C_6H_5·C(CN):NO·ONa.								
22	8;	1·52	−10°; 1 hr., then room; 15 mins.	6·2	—	—	89·7	4·1
23	17·4;	1·480	+14°; 60 ,,	19·35	—	—	80·1	0·55
24	13;	1·480	+15°; 60 ,,	19·45	—	—	80·0	0·55
(3) C_6H_5·CO·CN.								
25	13;	1·480	−10°; 1 hr., then room; 15 mins.	99·9	—	—	0	0·1
26	8;	1·52	−10°; 1 hr., then room; 1 hr.	19·2	—	—	10·0	70·8
(4) m-C_6H_4Br·CO_2H.				Unchanged.			Nitrated in p(o).	Nitrated in m.
27	148;	1·480	16·2°; 7 days	0	—	—	96·2	3·8
28	119	,,	room; 5 weeks	0	—	—	95·6	4·4
29	148	,,	16·2°; 24 hrs.	48·9	—	—	49·1	2·0

The corresponding yields by weight, together with explanatory remarks, will be found in the experimental part.

V. *The Constitution of Phenylbromocyanonitromethane and Other Acylmethyl Halides.*

The surprising reactivity of bromine in bromomalonic esters, compared with bromonitroacetic esters, led Willstätter and Hottenroth (*Ber.*, 1904, **37**, 1775) to propose formula (I) for the halides of secondary nitro-compounds and (III) for polynitro-compounds, (II; R″ = H) being retained for the halides of primary nitro-compounds.

$$\underset{R''}{\overset{R'}{}}\!>\!C\overset{O}{\frown}N\cdot OHal \qquad \underset{R''}{\overset{R'}{}}\!>\!C\!<\!\underset{NO_2}{\overset{Hal}{}} \qquad (NO_2)_2C\overset{O}{\frown}N\cdot O\cdot NO_2$$

(I.) (II.) (III.)

(IV.) $(NO_2)_3C\cdot O\cdot NO$ $C(NO_2)_4$ (V.)

Schmidt (*Ber.*, 1919, **52**, 402) then substituted for (III) an equilibrium formula (III $\rightleftharpoons$ IV), but later (with Ascherl and Knilling, *Ber.*, 1926, 59, 1876) reverted to (V) for polynitro-compounds and to (II) for all halogenonitro-compounds, following their discovery that methyl hypobromite is added to *cyclo*hexene in methyl-alcoholic solutions, not only of brominated secondary nitro-compounds, but also of tribromophenol bromide, etc., and that in particular dibromo- and bromonitro-malonic esters behave similarly. Now this similarity (" gleichartiges Verhalten ") was found in the fact that, *ceteris paribus*, the dibromo-ester gave 11·2% of hypobromite addition in 72 hours, whereas the bromonitro-ester gave 78·8% in 24 hours (thus reacting, roughly, at a fifty times higher bimolecular rate). Assuming, however, that in spite of such differences these authors' uniform formulation of all the compounds was justified, then they would all be *O*-bromides (hypobromites), since for one of them, tribromophenol bromide, this constitution may now be regarded as definitely proved (compare Lauer, *J. Amer. Chem. Soc.*, 1926, **48**, 442); a conclusion which would be extremely improbable in the case of, *e.g.*, dibromomalonic ester.

Willstätter and Hottenroth thought that *both* forms of bromonitromalonic esters might be accessible. We suggest that sometimes only the *C*-bromide may be stable, sometimes only the hypobromite form; in other cases both forms may exist in appreciable quantities in equilibrium—the relative stability of either being determined by the usual three factors (*p*, *q*, and *s*; compare previous papers). *Ceteris paribus*, *C*-Hal and *C*-NO_2 are much more stable than *O*-Hal and *O*-NO_2 (*p*). " Negative " substitution of *C* reduces this advantage (*p*), in the order $NO_2 > CN > CO$. Steric obstruction at *C* (*e.g.*, by C_6H_5) also reduces it (*s*). But if these effects happen to coincide with the possibility of a better affinity exchange in the *O*-form (*q*), then the resulting advantage may be more or less completely shifted to the *O*-form. For instance, the *O*-form of tribromophenol bromide, being benzenoid, has a better affinity exchange than the quinonoid isomeride. Conversely, transition of dibromomalonic ester into its *O*-form produces, in an ethylenic bond, a new centre of unsaturation. In a bromonitro-compound, however, a " double " bond is obviated in the *O*-form by means of an oxygen bridge. Similar considerations apply, *mutatis mutandis*, to transitions of the ketonic into the enolic forms of the corresponding hydrogen compounds. This may explain the observation of Thorpe and his co-workers (J., 1921, **119**, 1203; 1922, **121**, 1898), that from a *C*-bromide a hypobromite reaction was obtained in proportion to the tendency towards tautomerism exhibited by the corresponding hydrogen

compound.* Examining the results of Schmidt's experiments,† we found that the hypobromites (*e.g.*, tribromophenol bromide, bromonitromalonic ester) reacted most quickly, *C*-bromides incapable of tautomerism (*e.g.*, carbon tetrabromide, tribromoacetic ester) did not react, and other *C*-bromides reacted at relative rates parallel to the relative rates of partial transition into hypobromites which the considerations we have outlined would lead one to expect. In Willstätter and Hottenroth's case, a solution of bromonitroacetic ester should contain, not form (II) only as they assume, but both *C*- and *O*-forms. We find that their own experiments confirm this view. Whereas one of their comparative tests—substitution of hydrogen for bromine by means of dry ammonia or amines—was not conclusive, similar abnormal reduction by potassium iodide took place not only with bromonitromalonic, but also with bromonitroacetic ester; completely with the former (*O*-bromide), but only partly with the latter (*O*- + *C*-bromides).

We have applied Willstätter's tests to phenylbromocyanonitromethane and its *m*-nitro-derivative, in both of which dry ammonia rapidly and completely replaces bromine by hydrogen. *m*-Nitrophenylbromocyanonitromethane, a well-defined crystalline material, can, as such, be a hypobromite *only*. Semi-quantitative measurements of the rate of reduction of phenylbromocyanonitromethane, an oil, prove that it also consists of only one form, unless the rate of isomerisation of any *C*-bromide present were almost infinitely greater than Schmidt's and Willstätter's experiments indicate. Both compounds are also—instantaneously and quantitatively—reduced by potassium iodide. For comparison, an undoubted *C*-bromide of perfectly analogous composition, *viz.*, phenylbromomalonic ester, was examined. It gave a measurable reaction neither with ammonia nor with potassium iodide, thus placing the hypobromite structure of phenylbromocyanonitromethane beyond doubt. By heating with aniline, bromine was slowly replaced, the

* Several authors have failed to distinguish between the *abnormal* reduction of halogen compounds (by alkali iodides, amines, etc.), and *normal* reactions, such as their reduction by ordinary reducing agents (hydriodic acid, hydrazine, etc.) or the replacement by hydrogen of CO_2R, CO_2H, or CN (*via* CO_2H). Although in the latter replacements *reactivity* depends on the same three factors, the *nature* of the reactions is normal, carbonate being normally formed in preference to formate. Accordingly they can occur when not only these groups, but also the hydrogen which replaces them, is incapable of tautomeric migration (*e.g.*, elimination of carbonic acid from 2 : 4 : 6-trinitrobenzoic acid by mere boiling with water).

† Schmidt and his co-workers have recognised the existence of a hydrolytic equilibrium, but their formulation of it, *e.g.*, (in alcohol) $(NO_2)_3CBr + ROH \rightleftharpoons (NO_2)_3CH + ROBr$, is inadequate, since it ignores the real reactants on either side—the bridged *O*-bromide and the *iso*nitro-compound.

ratio of bromide to hypobromite reaction being about 6 : 1. Taking into account the much greater reactivity of the *O*-bromide, it is again obvious that its concentration in equilibrium with the *C*-bromide must be exceedingly small.

Our finding that the " true " form of phenylcyanonitromethane, for which we postulate an equilibrium between the usual nitro- and the bridge formulation, can change to benzoic acid without passing through the *iso*nitro-form supports our conception of the presence of a bridged constituent. More conclusive proof which we have obtained will be presented in connexion with other work.*

VI. *Interpretation by Theories of Aromatic Substitution.*

The transformation of phenylbromocyanonitromethane into its *m*-bromo-isomeride constitutes, we believe, the first proved case of *intramolecular m*-migration of a lateral *substituent.* It makes it probable that the change of benzoyl nitrate into *m*-nitrobenzoic acid observed by Francis (*Ber.*, 1906, **39**, 3798) and of tribromophenol bromide into tetrabromophenol (Benedikt, *Annalen*, 1879, **199**, 132) are also intramolecular and, together with the almost exclusive extramolecular *m*-nitration of phenylbromocyanonitromethane, proves that the law governing direct and indirect *m*-substitution is the same—just as one and the same law has long been known to apply to direct and indirect substitution in the *o*- and *p*-positions. *m*-Substitution in these cases agrees with our theory of affinity distribution, as well as with Robinson's electronic theory; with the former because of the postulated inversion of the directive effect of methyl through the affinity demand of tervalent nitrogen; and with the latter in view of the postulated electron shift toward the " negative " groups.

Again, the essentially exclusive *p*-suhstitution of phenylcyano-*iso*nitromethane follows, according to our theory, from the greatly enhanced residual affinity of the methyl carbon. It can also be reconciled with Robinson's views on the assumption that nitration (even with acid of *d* 1·52) occurs essentially only in a—temporary—conjugated phase, and not in the—relatively permanent—normal phase in which the electron shift would cause *m*-substitution as above.

Lastly, several mechanisms in accordance with either theory can be devised for the partial oxidation of phenylcyanonitromethane to

* Branch and Jaxon-Deelman (*J. Amer. Chem. Soc.*, 1927, **49**, 1765) allot the bridge form to the *iso*nitro-compound, and the nitronic formula to its salt (ion). In Part X of this series we shall give definite experimental proof that this view is untenable, and shall show that these authors' experiments afford valuable proof for our own formulation.

p-nitrobenzoic acid and for the partial thermal decomposition of phenylbromocyanonitromethane into *p*-nitrobenzoyl cyanide; but none can be proved at present.

EXPERIMENTAL.

In the first series of nitrations, the old tedious method of separating the acids by fractional crystallisation was used. When it was found that bromo- and nitrobromo-acids were present, and that these precluded strictly quantitative separations, our new method was evolved and applied in a further series of nitrations. Then the unexpected discovery that oxidation was accompanied by further *p*-nitration made it necessary to repeat all the nitrations and oxidise the products by a new method, so that altogether 61 nitrations and separations were carried out. We shall—apart from a few special cases—confine ourselves to recording *full* data of the final series only.

I. *Methods.*—(1) *Preparation of phenylbromocyanonitromethane.* (a) To an ice-cooled solution of sodium phenylcyano*iso*nitromethane (1 part) in water (5—6 parts), bromine (0·86 part; 0·99 equiv.) in saturated, ice-cooled aqueous solution was added all at once, with stirring. Average yield = 1·275 parts of phenylbromocyanonitromethane = 97 mol.%.

(b) To the salt (1 part) in water (20 parts), bromine (0·7 part; 0·8 equiv.) in water (70 parts) was added at 0° during 45 minutes with mechanical stirring.

(c) With hypobromous acid: To the salt (3·68 parts) in water (100 parts), a solution of potassium hydroxide (2·24 parts) and bromine (3·20 parts) in water (180 parts) was added at 0°, followed rapidly, with mechanical stirring, by concentrated sulphuric acid (1·96 parts) in water (50 parts). Yield 4·43 parts of phenylbromocyanonitromethane = 92 mol.%.

In all cases the precipitated oil was extracted with pure ether, and the dried ethereal solution evaporated without heating. Beyond variations in the yellow colour, no differences could be detected between these different preparations, but method (A) was used throughout, except for nitration No. 18, where method (C) was employed. An attempt to prepare phenylbromocyanonitromethane from the free *iso*nitro-compound by adding, at 0° and with good stirring, 0·367 g. of 10% sulphuric acid to 1·38 g. of the salt in 138 c.c. of water, and then at once, to the still clear solution, 120 c.c. of 1% aqueous bromine, yielded a product containing only 27·4% of bromine instead of 33·2%.

(2) *Nitration.* During addition of phenylbromocyanonitromethane to the nitric acid the temperature was not allowed to rise more than 1°. The mixture was poured on 270 parts of chopped

ice per part of phenylbromocyanonitromethane used and was extracted with 54 parts, then again with 27 parts, of pure ether, and the extract was washed four times with 18 parts of water—or, where the acids were extracted, only twice with water and twice with an excess of concentrated aqueous potassium bicarbonate—then at once dried and evaporated at the ordinary temperature.

(3) *Determination of bromine.* (a) In the side chain: 1 Part of nitrated oil in 20 parts of benzene was shaken with 4 parts of potassium iodide in 20 parts of water and immediately titrated with $N/10$-thiosulphate, starch being added when the solution had become very light brown, and the mixture being well shaken during titration. With pure phenylbromocyanonitromethane and *m*-nitrophenylbromocyanonitromethane there was no need to dissolve the product in benzene before treatment. (b) In the nucleus: In the acids obtained by oxidation, bromine was determined by the Carius method.

(4) *Oxidation.* Method A: 1 Part of the nitrated material was heated with 1·13 parts of permanganate in 34 parts of water; as soon as the mixture boiled, 0·38 part of caustic soda in 9·5 parts of water was added. On decolorisation, further permanganate was added in lots of 0·38 part until the colour persisted after 3 hours' boiling.

Method B: 1 Part of the nitrated material was treated on a shaking machine with 7·76 parts of 10% aqueous caustic potash and 7·76 parts of water for 1 hour, and then, after dilution to 120 parts, boiled with 2 parts of permanganate. The end-point was reached as in method A.

Method C: Exactly as B, except that shaking was continued for 3 hours.

Method D: The same, but with 6 hours' shaking.

Throughout, the acids were brought to constant weight at 50°.

(5) *Determination of the different nitro-acids.* The method we have evolved is so simple, accurate, and of such general applicability that we describe it in a separate communication (Part VI; preceding paper). Here it suffices to say that benzoic and *m*-bromobenzoic acids are together recovered as such (see Part VI for calculation of their molecular percentages); that *p*- and *o*-nitrobenzoic acids are together weighed as 2 : 4 : 6-tribromoaniline, and *m*-nitrobenzoic acid as 2 : 4 : 6-tribromo-3-aminobenzoic acid, whereas 4-(and/or 2-)nitro-3-bromobenzoic acid is weighed as tribromoaniline derived from a separate fraction.

II. *Results of the Nitrations.*—Table III contains the actual weighings in connexion with all nitrations where oxidation was carried out by a method precluding re-arrangement. This applies

to all oxidations by methods C and D, also by method B whe applied *to 10-day nitrations* (where little material capable of re arrangement survived), and by method A in the case of complet nitration. Beside these, nitrations 4, 8, 13, and 15, where oxidatio involved some, but relatively little, migration, have been include for comparison; the corresponding yields of tribromoanilin (marked with asterisks), when compared, respectively, with those c Nos. 3, 7, 12, and 14, show the amount of migration during oxidatior In Table II, the corresponding figures with asterisks represent th *true* molecular $p(o)$-nitration as determined by Nos. 7, 12, and 14 respectively, and *have been used in calculating* the remainin molecular yields in Nos. 8, 13, and 15. A bar in the tables signifie that a determination was not carried out. The experimental cor ditions for each nitration in Table III are to be found under th corresponding numbers in Table II.

The recovery of material after nitration was practicall quantitative throughout; but since the time during which th *viscous oils produced from phenylbromocyanonitrom*ethane b treatment with nitric acid of *d* 1·480 could be kept in a vacuun desiccator was limited by their tendency to lateral decomposition traces of ether were sometimes retained, and therefore the potassiun iodide determinations of lateral bromine in the nitration product are only approximately quantitative; all other determinations ar unaffected, since they depend only on the acids.

The purity of the compounds obtained by reduction and bromi ation of the acids was always checked by melting- and "mixed *melting-point determinations. For tribromoaniline from p(o)-nitr* benzoic acid, melting points ranged between 113—117° and 118—119° (m. p. of pure substance, 119—120°); for tribromoanilin from bromonitrobenzoic acid, between 105—110° and 114 to 117° and for tribromoaminobenzoic acid (when more than traces wer obtained), between 164—167° and 170—171° (m. p. of pure acid 170·5°). The m. p. of the benzoic acid naturally varied with it content of bromobenzoic acid; for example, in No. 4 (brief nitratior the acid melted at 117—119° (m. p. of pure acid, 121°).

The percentages of nuclear bromine for Nos. 1 and 5 were obtaine respectively, from duplicate nitrations 2 and 6.

In No. 17, 5·300 g. of pure *m*-nitrophenylbromocyanonitro methane were first separated by recrystallisation of the solid portio (9·063 g.) of the nitration product, and corresponding fractions of th oily portion (0·669 g.) and the material from the mother-liquor were then oxidised together. In a duplicate nitration, 0·400 g. c oil and 3·856 g. of solid (m. p. 67—69°) were obtained, yieldin 2·086 g. of pure *m*-nitrophenylbromocyanonitromethane. From th

Nitration No.	Material used (g.).	Yield (g.).	Acids extracted by $KHCO_3$.	Oxidised (g.).	Yield of acids (g.).	Br in acids (%).	Reduction and bromination of acids. Used (g.).	Found (g.). Benzoic + bromobenzoic acids.	Found (g.). Tribromoaniline from *p*(*o*)-nitro-acid.	Found (g.). Tribromo-*m*-aminobenzoic acid.	Found (g.). Tribromoaniline from nitro-*bromo*-benzoic acid.	Lateral Br in nitration product (% of theory by weight).	Oxidation method.
1. PBCN.													
1, 2	5·567	5·501	—	4·033	1·970	1·58	1·000	0·901	0·092	0·006	—	94·1	C
3	6·702	6·801	—	6·142	2·041	2·28	1·000	0·915	0·073	0·015	—	94·8	D
4	11·770	11·809	—	10·410	5·061	2·02	1·500	1·340	0·254*	0·007	—	90·7	B
							1·000	0·880	0·155*	0·005	—		
5, 6	5·260	5·140	+ 0·017	4·477	2·212	2·4	1·000	0·905	0·085	0·020	0·006	92·4	C
7	6·500	6·329	+ 0·149	5·448	2·889	11·69	1·000	0·818	0·102	0·044	0·103	69·0	D
8	6·232	8·284	—	7·681	4·146	11·97; N = 1·18	1·000	0·703	0·162*	0·012	0·101	62·0	B
9	5·322	5·334	+ 0·044	4·624	2·554	10·5	1·000	0·085	0·120	0·325	0·092	64·1	C
10	8·310	7·201 +		3·037	1·820	19·51	0·500	0·350	0·039	0·056	0·097	46·7	D
			0·811	—	—	15·2	0·554	0·373	0·120	0·072	0·071	0	—
11	9·130	7·878 +		2·365	1·485	21·29	1·000	0·773	0·073	0·112	0·216	44·9	C
			0·812	—	—	15·8	0·500	0·344	0·101	0·059	0·063	0	—
12	8·189	5·883	—	4·160	2·514	23·4; N = 2·04	1·000	0·713	0·075	0·030	0·301	31·8	B
							0·800	—	0·058	0·021	0·231		
13	2·521	2·403	—	1·927	1·107	25·4; N = 2·04	0·465	0·390	0·088*	0·006	—	—	A
14	6·070	5·500	—	4·924	2·983	24·8; N = 2·5	0·900	0·524	0·086	0·064	0·326	23·0	B
15	9·800	9·091	—	7·340	4·925	24·3; N = 2·61	1·000	0·805	0·114*	0·080	0·307	19·6	A
							1·000	0·582	0·128*	0·075	0·335		
16	5·060	5·170	—	4·392	2·311	9·17	1·000	0·502	0·105	0·827	0·072	73·0	C
							0·800	0·357	0·085	0·623	0·058		
17	8·340	9·732	—	4·099	1·865	—	1·000	0	0·301	1·830	—	—	A
18	8·000	10·411	+ 0·149	2·602	1·352	—	1·000	91	0·154	2·003	—	—	C
19	5·011	5·448	+ 0·176	3·604	1·752	—	1·000	0·308	0·125	1·372	—	—	C
20	8·925	8·669	+ 0·148	3·088	—	—	1·000	—	0·044	0·051	—	—	C
21	5·011	4·872	+ 0·064	1·645	0·771	—	0·700	0·624	0·030	0·044	—	—	C
2. $C_6H_5·C(CN):NO·ONa$.													
22	3·000	Oil	+ 0·277	Whole oil	2·221	0	1·000	0·044	1·800	0·102	0	0	C
23	6·000	5·282	KOH-soluble oxid.		3·357	0	1·000	0·076	1·804	0·012	0	0	C
			KOH-insol. oxidised.		0·564	0	0·400	0·217	0·287	0·007	0		
24	6·000	5·029	+	2·330	1·569	0	1·000	0·169	1·634	0·015	0	0	C
			0·739	—	—	0	0·700	0·041	1·290	0·004	0		
3. $C_6H_5·CO·CN$.													
25	4·436	4·293	—	0·642	0·552	0	0·545	0·510	—	0·008	0	0	See text
26	5·410	7·051	—	6·600	5·189	0	1·000	0·102	0·207	1·673	0	0	
4. *m*-$C_6H_4Br·CO_2H$.													
27	0·500	0·610	—	—	—	—	0·610	0	0	0·043†	0·794	0	—
28	0·500	0·613	—	—	—	—	0·400	0	0	0·030†	0·498	0	—

oxidation-acids of the remainder, 15·9% of *p*-nitrobenzoic acid was isolated, corresponding to 7—8 mol.% of pure *p*-acid on the whole nitration product. *o*-Nitration must therefore be negligible.

In No. 22, the composition of the acids (only 0·277 g., m. p. 227—231°) given had to be based on the analysis of the acids in No. 24, of equal melting point.

No. 22 was duplicated, but with addition of 1 g. of sodium nitrite to the nitric acid to see whether the proportion of acids produced during nitration was due to the content of nitrous acid. This is not the case, since only 0·253 g. of acids (m. p. 222—227°) was formed. In a duplicate of No. 9, but at 16·2° instead of 12·6°, and with 0·3 g. of sodium nitrite per g. of phenylbromocyanonitromethane added, there was a slightly higher acid formation (2·4% of the weight of phenylbromocyanonitromethane, against 0·8% in No. 9).

In a triplicate of No. 22 and in a duplicate of No. 23, after removal of acids in bicarbonate, the remainder, in benzene, yielded a precipitate of ammonium salt, and its KOH-soluble portion gave a KI-soluble hypobromite; the presence of much material with an *unaltered side chain* (see Table II) thus being confirmed.

In No. 24, to correlate the molecular percentages of the acid fractions produced during nitration and by oxidation, a normal oxidation yield of 85% of the theoretical was taken as a basis.

In Nos. 25 and 26, oxidations were carried out with a 1 : 60 permanganate solution as described in Part V of this series.

In No. 25, the yield of 4·293 g. was separated into 3·651 g. of pure unchanged benzoyl cyanide (m. p. 33—34°) and a partly oily fraction, only the latter being submitted to oxidation.

In Nos. 20 and 21, the nitration products, instead of being shaken with bicarbonate, were extracted five times with sodium carbonate according to Baker and Ingold's directions, but even so, not 10% as they state, but only 1 to 2% of acids were obtained.

In Nos. 27, 28, and 29, the traces of *m*-nitro-compound (marked †) were presumably recovered as tetrabromo-*m*-aminobenzoic acid. The percentage of this in No. 29 had to be deduced from Nos. 27 and 28. The *m*-bromobenzoic acid used, after repeated crystallisation, always had the (*usually* obtained) m. p. of 152—153° (not 155°; Wheeler and McFarland).

In No. 13, the 0·390 g. of benzoic, etc., acids yielded, by fractional recrystallisation from water, 0·160 g. of *m*-bromobenzoic acid (m. p. 143—145°; mixed m. p. 152·5—153°) and, on further recrystallisation, 0·045 g. melting at 148—156° (nitrobromo-acids; m. p. depression with *m*-bromobenzoic acid). The 0·160 g. of *m*-bromo-acid isolated, although not quite pure, represents quite

75% of the total unnitrated bromo-acid formed. In a duplicate of No. 13, on 8·353 g. of phenylbromocyanonitromethane, the oily nitration product, on standing, deposited first nitration acids, from which, by 50% methyl alcohol, 0·2 g. of *m*-bromobenzoic acid (m. p. 147—150°; mixed m. p.) was obtained, and then crystals, m. p. 167—180°, yielding on treatment with benzene 0·1 g. of *p*-nitrobenzoic acid (m. p. 190—200°; mixed m. p.).

In Nos. 10 and 11 (figures for No. 11 in brackets), the KI-insoluble portion from 3·986 (4·475) g. of the nitration product yielded, by method D(C), 1·259 (1·545) g. of acids containing 23·44 (26·1)% of bromine. Of these, 0·900 (1·000) g. gave 0·581 (0·693) g. of benzoic + bromobenzoic acids, 0·035 (0·045) g. of tribromoaniline from *p*-nitro-acid, 0·331 (0·322) g. of tribromoaniline from nitrobromo-acid, and 0·030 (0·035) g. of tribromo-*m*-aminobenzoic acid. Before oxidation, the material smelled strongly of benzoyl cyanide.

The diluted spent acids from two nitrations with 13 parts of nitric acid of *d* 1·480, one at 15° for 24 hours, the other at 16·2° for 4 days, gave with silver nitrate at first only a faint cloudiness, but in the course of several minutes a very material precipitation of silver bromide. Since bromine reacts instantaneously under similar conditions, this test appeared to confirm the postulated presence of hypobromous acid.

III. *Other Observations.*—1. *Purity of phenylbromocyanonitromethane.* Repeated oxidations of phenylbromocyanonitromethane by method C (p. 471) yielded benzoic acid containing from 0·40 to 0·57% of halogen, calculated as bromine, so that phenylbromocyanonitromethane (prepared by method A; p. 471) contains 0·20 to 0·29%. This is, at least partly, due to re-arrangement in ethereal solution (see below) during its preparation, but there may, in addition, be a trace of nuclear bromination during the action of bromine on the sodium salt. The salt we used contained only 0·066% of chlorine (derived from a trace of nuclear chlorine in the benzyl chloride from which it was made), which accounts for 0·085% in phenylbromocyanonitromethane, calculated as bromine.

The potassium iodide method showed an average content of hypobromite-bromine of 99·2% of the theoretical for the samples of phenylbromocyanonitromethane used in the recorded experiments, with variations between 98·8 and 99·4%—except in No. 18 (phenylbromocyanonitromethane made by means of hypobromous acid: KI-soluble Br, 98·0%).

2. *Volatility and stability of phenylbromocyanonitromethane.* The substance (3·623 g.) was dissolved in 45 c.c. of commercial "absolute" ether (*d* 0·717) and, after the ether had been removed by a current of dry air, was brought to constant weight in a vacuum;

loss, 0·019 g. = 0·52%. The percentage of mobile bromine, originally 99·4, was finally 98·6.

When phenylbromocyanonitromethane was left for 1 week in a desiccator over caustic potash, at atmospheric pressure, the mobile bromine decreased by 2%, but the percentage of nuclear bromine determined after oxidation showed no measurable change.

3. *Re-arrangement of phenylbromocyanonitromethane in ether.* The substance (6·330 g.), in 63·2 c.c. of ether (carefully dried over sodium), was left for 48 hours at room temperature. Whereas initially 2·133 g. of the phenylbromocyanonitromethane had yielded 0·954 g. of acids containing 0·40% of bromine, 5·080 g. of the recovered phenylbromocyanonitromethane gave on oxidation by method C 2·356 g. of acids containing 1·60% of bromine, corresponding to a migration of 0·6% of bromine, involving a re-arrangement of 1·8% of the phenylbromocyanonitromethane. Simultaneously the mobile bromine decreased from 98·8% to 97·0%.

When phenylbromocyanonitromethane was treated in exactly the same way, except that 93% of its weight (= 1·7 equivs.) of benzoyl cyanide was initially added to the solution in ether, 0·48% of the bromine migrated in 48 hours; there was therefore no bromination of benzoyl cyanide.

4. m-*Nitrophenylbromocyanonitromethane.* The solid portion amounting to over 90% of the total nitration products, obtained with nitric acid of *d* 1·52, and melting usually at 67—69°, was dissolved in a little cold benzene and allowed to crystallise after addition of petrol; 55—60% of the solid was thus recovered as pure m-*nitrophenylbromocyanonitromethane*, white needles, m. p. 70—70·5°, which did not change on further recrystallisation (Found: N, 14·90; Br by the Carius method, 27·78; Br by treatment with potassium iodide, 27·5, 27·6. $C_8H_4O_4N_3Br$ requires N, 14·69; Br, 27·96%). For proof of the position of the nitro-group, see below.

5. *Reduction of phenylbromocyanonitromethane and its* m-*nitro-derivative by potassium iodide, potassium hydroxide, or ammonia.* That treatment with potassium iodide (see I, 3; p. 471) actually yields the potassium salt of the corresponding *iso*nitro-compound was proved by reconverting this salt into the hypobromite. For example, the aqueous solution of the salt obtained from *m*-nitrophenylbromocyanonitromethane by treatment with sodium iodide gave, after removal of the iodine in benzene and gradual addition of a little less than the theoretical amount of a 1% bromine solution at 0°, a precipitate of *m*-nitrophenylbromocyanonitromethane (m. p. 67—68°; mixed m. p.) amounting to 85% of the theoretical quantity, calculated on the bromine used.

With an excess of 10% aqueous caustic potash, phenylbromo-

cyanonitromethane and its *m*-nitro-derivative rapidly gave, on shaking, solid *iso*nitro-potassium-salt, which dissolved on addition of water.

Sodium carbonate in concentrated solution did not react immediately with phenylbromocyanonitromethane on shaking, but reacted partly on standing for a week.

Phenylbromocyanonitromethane in ether, when shaken with an excess of 10% aqueous ammonia, reacted rapidly with a strong evolution of gas (presumably nitrogen). Solid *m*-nitrophenylbromocyanonitromethane reacted similarly with aqueous ammonia, practically everything going into solution.

Baker and Ingold, who used potassium hydroxide to nearly neutralise their nitration mixture, thereby presumably reduced some of the supernatant material; this would account for their low nitration yields, which they attributed to oxidation.

Dry ammonia gas, passed into a benzene solution of phenylbromocyanonitromethane, precipitates most, but not nearly all, of the material in the form of the *iso*nitro-ammonium salt, together with some ammonium bromide derived from the decomposition of nitrogen bromide, entirely in accordance with Willstätter and Hottenroth's observations on bromonitromalonic esters. We found, however, that the incompleteness of the precipitation is merely due to solubility or dissociation of the ammonium salt in benzene, since separation from petrol is practically complete. The precipitate was removed at intervals of 4 minutes, and the filtrate brought to its original volume, dry apparatus of approximately constant dimensions being used throughout. The precipitates were brought to nearly constant weight in a vacuum, and the bromide ion in each was determined and deducted as ammonium bromide. Thus 2·063 g. of phenylbromocyanonitromethane in 60 c.c. of petrol (b. p. 30—50°) gave 0·889, 0·348, 0·269, and 0·114 g. at 4-minute intervals and finally 0·112 g. in 30 minutes: total, 1·732 g. of ammonium salts; the excess of 0·209 g. over the theoretical quantity being due to occluded solute. The ammonium bromide precipitates amounted to 0·372 g., and the petrol finally retained 0·078 g. of solute. In two other experiments, 2·026 g. of phenylbromocyanonitromethane gave 1·859 g. of ammonium salt (theory requires 1·605 g.), and 1·686 g. gave 1·481 g. (theory, 1·252 g.), whereas 0·604 g. of phenylbromocyanonitromethane made with hypobromous acid gave 0·438 g. (theory, 0·448 g.) in 30 minutes. For a two-phase reaction, and allowing for occlusions, the rate of change follows the mass law sufficiently to preclude the initial presence of an appreciable proportion of a relatively inert isomeride.

m-Nitrophenylbromocyanonitromethane (0·500 g.), dissolved in

10 c.c. of dry benzene, gave with dry ammonia in 2 minutes 0·365 g. of ammonium salt and 0·052 g. of ammonium bromide. The filtrate, evaporated in a vacuum and redissolved in 3 c.c. of benzene, gave 0·013 g. of ammonium salt and 0·010 g. of ammonium bromide: total ammonium salt, 0·378 g. (theory requires 0·389 g.).

0·50 G. of crude *m*-nitrophenylbromocyanonitromethane (m. p. 67—69°) in 10 c.c. of benzene, after prolonged treatment with ammonia gas, gave 0·455 g. of precipitate; the filtrate retained 0·027 g. of an oil. A filtered solution of the 0·455 g. in 20 c.c. of water, treated at 0° with an excess of 3% aqueous bromine, gave 0·372 g. of *m*-nitrophenylbromocyanonitromethane (shrinking at 67°, m. p. 69—70°; mixed melting point), thus proving that dry ammonia produces the ammonium salt of *m*-nitrophenylcyano*iso*-*nitromethane*.

6. *Decomposition of phenylbromocyanonitromethane by heat alone.* One of us (*loc. cit.*) had stated that phenylbromocyanonitromethane decomposes "at water-bath temperature"; Wislicenus and Schäfer (*loc. cit.*) then gave "about 55°" as the decomposition point with strong gas evolution. A number of samples prepared by methods (a) and (b) (p. 470) have now been examined. All the samples gradually darkened, but evolution of gas first occurred at 72—78° with slow heating, and at 80—83° in a bath pre-heated to 75°; a further rise of 2—3° made the evolution violent.

Quantitative tests: (a) Phenylbromocyanonitromethane (3·740 g.) was heated at 90—100° until the gas evolution had ceased, and the residue was shaken for 1 hour with 60 c.c. of cold 5% aqueous potassium hydroxide, and oxidised with a 1 : 60 permanganate solution. The acids (1·739 g.) contained 0·47% of bromine, that is no more than acids obtained from phenylbromocyanonitromethane by oxidation method C (p. 471), so that no bromine had migrated during decomposition. 1 G. of the acids gave on reduction, etc. 0·869 g. of benzoic acid and 0·209 g. of tribromoaniline.

(b) Phenylbromocyanonitromethane (24 g.), similarly heated left a residue of 12·50 g. At 4 mm. pressure this gave a distillate of 9·38 g. of benzoyl cyanide (m. p. 32—34°) and a residue of 2·30 g. which, on recrystallisation from petrol (b. p. 100—120°), yielded 1·150 g. of *p*-nitrobenzoyl cyanide (m. p. 114—115°) + 0·173 g (m. p. 104—108°); the mother-liquor contained some benzoyl cyanide.

(c) Phenylbromocyanonitromethane (19 g.) was treated as under (b), but the residue in the flask was distilled (at 100—120°/4 mm.) before recrystallisation from petrol (b. p. 60—80°). Distillate 0·9 g.; m. p. 103—108° before and 115—116° after recrystallisation.

(d) Phenylbromocyanonitromethane (15 g.) was treated as under (c), except that decomposition was effected in an atmosphere of carbon dioxide. The crude distilled *p*-nitrobenzoyl cyanide (m. p. 101—106°) weighed 0·8 g. The constant m. p. after recrystallisation was 115·5—116° (Found: N, 16·28, 16·08. Calc. for $C_8H_4O_3N_2$: N, 15·91%). The result shows that the oxygen needed for the formation of *p*-nitrobenzoyl cyanide *does not* come from the air.

p-Nitrobenzoyl cyanide has already been obtained, by another method, by Zimmermann (*loc. cit.*), who gives the melting point as 116·5°. We found that atmospheric moisture gradually changes it to *p*-nitrobenzoic acid.

7. *Decomposition of* m-*nitrophenylbromocyanonitromethane by heat alone.* This substance begins to evolve gas slightly above its melting point, or, on prolonged heating, even at its melting point. Quantitative tests: 8·00 g. heated to constant weight, at about 95°, in a long-necked flask provided with a calcium chloride tube, showed a loss of 2·70 g. The product, distilled at 7 mm. pressure, gave 4·60 g. of *m*-nitrobenzoyl cyanide, distilling at 144—146°, and 0·65 g. of residue, from which alcohol extracted 0·468 g. of a semi-solid of high bromine content, leaving 0·106 g. of a bromine-free solid melting above 200°.

m-Nitrobenzoyl cyanide was obtained by us as a light yellow oil (Found: N, 15·98. Calc. for $C_8H_4O_3N_2$: N, 15·91%). Like its *p*-isomeride, it is gradually hydrolysed to the corresponding nitrobenzoic acid by atmospheric moisture. 1·116 G., when boiled with 24 c.c. of 10% sulphuric acid for 3 hours, gave 1·058 g. (quantitative yield) of *m*-nitrobenzoic acid (m. p. 138·5—139°; mixed m. p.).

8. *Changes in presence of heated aqueous permanganate.* (a) Phenylbromocyanonitromethane (4·255 g.) was heated with 4 g. of permanganate in 240 c.c. of water for 1 hour, then with a further 2 g. of permanganate for 3 hours. The acids formed (1·776 g.) contained 0·85% of bromine; 1 g. thereof gave on reduction, etc., 0·794 g. of benzoic + bromobenzoic acids and 0·316 g. of tribromoaniline, and therefore consisted of 2·1% (by weight) of bromobenzoic, 16·0% of *p*(*o*)-nitrobenzoic, and 81·9% (by difference) of benzoic acids. In a parallel test, 5·530 g. of phenylbromocyanonitromethane gave 2·369 g. of acids containing 0·91% of bromine, of which 1 g. yielded 0·804 g. of benzoic + bromobenzoic acids and 0·334 g. of tribromoaniline.

(b) Phenylcyanonitromethane, obtained from 2 g. of its sodium salt, dissolved in water, and 10·9 c.c. of *N*-sulphuric acid, was, after dilution to 120 c.c., boiled with 2 g. of permanganate until this was decolorised, and then with a further 2 g. for 2 hours. The acids

(1·503 g.) yielded 1·147 g. of benzoic acid and 0·549 g. of tribromoaniline, corresponding to 18·5% (by weight) of *p*(*o*)-nitrobenzoic acid.

(c) The ammonium salt of phenylcyano*iso*nitromethane, obtained by passing dry ammonia for 20 minutes through a petrol solution of phenylbromocyanonitromethane, gave with a 1 : 60 solution of permanganate 0·403 g. of acids yielding 0·030 g. of tribromoaniline, corresponding to 3·75% (by weight) of *p*(*o*)-nitrobenzoic acid.

(d) The potassium salt of phenylcyano*iso*nitromethane, obtained by completely dissolving 3·228 g. of phenylbromocyanonitromethane by shaking it for 15 minutes with 50 c.c. of 5% aqueous potassium hydroxide and diluting the solution to 240 c.c., was oxidised by boiling with 4 g. of permanganate. The 1·434 g. of acids obtained yielded, besides benzoic acid of 0·57% bromine content, only 0·005 g. of tribromoaniline, corresponding to 0·17% (by weight) of *p*(*o*)-nitrobenzoic acid.

(e) Phenylbromocyanonitromethane in the presence of foreign matter gave on treatment with permanganate a higher degree of *p*-migration than phenylbromocyanonitromethane alone. For example, the phenylbromocyanonitromethane–benzoyl cyanide mixture recovered from the experiment described under (3) (p. 476) was oxidised (5·345 g.), as in 8 a (p. 479), to 3·763 g. of acids, 1 g. of which yielded 0·881 g. of benzoic acid and 0·200 g. of tribromoaniline, corresponding to 27·4% (by weight) of *p*(*o*)-nitrobenzoic acid calculated on the proportion of the acids corresponding to the phenylbromocyanonitromethane in the original mixture.

Again, the earlier nitration mixtures, oxidised by method A (p. 471) (oxidation of phenylbromocyanonitromethane in presence of products with an altered side chain), gave yields of tribromoaniline, of which the following are examples : nitration analogous to No. 1, 0·667 g. of tribromoaniline per g. of acid; analogous to No. 3, 0·671 g. of tribromoaniline; analogous to No. 3, 0·700 g. of tribromoaniline; analogous to No. 8, 0·513 g. of tribromoaniline. Phenylcyanonitromethane also gave more tribromoaniline when oxidised by method A in presence of admixtures; for instance, the benzene layer from the potassium iodide reaction of a nitration product obtained according to No. 8 gave, after oxidation by method A, 0·596 g. of tribromoaniline per g. of acid, and 0·850 g. in the case of a nitration with 13 parts of nitric acid of *d* 1·480 at − 11° for 1 hour and then at 15° for 15 minutes. The latter nitration yielded a nitration product giving, by method A, acid containing 38·2% of *p*(*o*)-nitrobenzoic acid, from which 26·2% (by weight) of *p*-nitrobenzoic acid (m. p. 228—232°) was isolated; 22%, m. p. 225—230°, was obtained in a duplicate nitration, an

18·2% (m. p. 230—235°) in another similar experiment (nitration, however, being effected with only 8 parts of nitric acid).

(f) *m*-Nitrophenylbromocyanonitromethane (0·500 g.), oxidised by method C (p. 471), yielded 0·252 g. of bromine-free *m*-nitrobenzoic acid (m. p. 139°; mixed m. p.). By method A, 0·610 g. yielded impure *m*-nitrobenzoic acid which gave the thiophen test of the corresponding glyoxylic acid.

To show that the mere trace of re-arrangement of the potassium salt of phenylcyano*iso*nitromethane corresponds to a mere trace of hydrolysis of the salt, 2 g. of the corresponding sodium salt, in 40 c.c. of water, were shaken for 15 minutes with 40 c.c. of benzene. On evaporation the benzene layer left only 0·015 g. of extracted hydrolysed material.

(g) *p*-Nitrobenzaldehyde (1·000 g.) was boiled for 3 hours with 1 g. of permanganate in 60 c.c. of water. Another 1·000 g. of the aldehyde was shaken for 3 hours with 8 c.c. of 5% potassium hydroxide, then diluted to 60 c.c. and, after addition of 1 g. of permanganate, boiled for 3 hours. The yield of *p*-nitrobenzoic acid in the first case was 0·942 g., m. p. 234—236°, and in the second case 0·941 g., m. p. 235—236°. Addition of potassium hydroxide according to method C, therefore, diminishes neither the yield nor the degree of purity of *p*-nitrobenzoic acid.

9. *Changes in presence of hot dilute nitric acid.* 1·645 G. of the nitration product of No. 21 (obtained according to Baker and Ingold's directions) were boiled, also according to their directions, with nitric acid (13·6 c.c.; *d* 1·125; 2 hours). The yield of acids was 0·904 g. From 0·900 g. of this, 0·688 g. of benzoic acid, 0·288 g. of tribromoaniline, and 0·077 g. of tribromo-*m*-aminobenzoic acid were obtained, corresponding to 16·2% (by weight) of *p*-nitrobenzoic acid and 3·82% of *m*-nitrobenzoic acid. On repetition, the yields were 15·75% and 3·62%, respectively (nitration No. 20). But here again, the true amount of *p*-nitrobenzoic acid due to nitration, as ascertained by method C (see Tables II and III), was only a small fraction of the above. The nitric acid used by Baker and Ingold, who found quite 52% of *m*-nitrobenzoic acid, must obviously have been substantially stronger than they indicate. Even at a higher temperature, relatively little *m*-nitration occurs with 8 parts of nitric acid of *d* 1·490. For instance, at + 15°, 4·400 g. of phenylbromocyanonitromethane yielded in 4 hours 4·426 g., including 0·062 g. soluble in bicarbonate, 2·840 g. of which, when oxidised with nitric acid as described above, gave 1·663 g. of acids; 1 g. of these yielded 0·655 g. of benzoic acid, 0·339 g. of tribromoaniline, and 0·399 g. of tribromo-*m*-aminobenzoic acid, corresponding to 17·2% (by weight) of *p*-nitro- and 17·8% of

m-nitro-benzoic acid. Since the amount of benzoic acid was found considerably to exceed that of its *p*-nitro-derivative, it appears difficult to account for Baker and Ingold's analysis of their oxidation product (49·6% of carbon, nitrobenzoic acid requiring 50·3, and benzoic acid 68·8%).

10. *Changes in concentrated sulphuric acid.* (a) *m*-Nitrophenylbromocyanonitromethane (0·4 g.), dissolved in 5 c.c. of concentrated sulphuric acid, immediately turned pale blue and became brown after 5 minutes. A solution of 1 g. in 10 c.c. of concentrated sulphuric acid, after being left for 24 hours at room temperature, was poured on ice (gas evolution) and extracted with ether; 0·711 g. was obtained which yielded, by two recrystallisations from benzene, 0·172 g. (m. p. 143—144°; depression with *m*-nitrobenzoic acid) (Found: N, 7·4. Calc. for *m*-nitrophenylglyoxylic acid, $C_8H_5O_5N$: N, 7·2%). In another similar experiment, 33% (by weight) of the *m*-nitrophenylbromocyanonitromethane was recovered as *m*-nitrophenylglyoxylic acid, m. p. 141—143°, and 144—145° after one recrystallisation from benzene containing a little alcohol. The acid gave the characteristic thiophen test. We obtained the same acid by leaving 1·970 g. of *m*-nitrobenzoyl cyanide with 10 c.c. of hydrochloric acid (*d* 1·195) at room temperature for 48 hours and filtering off the crystals. Yield 1·710 g., m. p. 139—143°; by recrystallisation from benzene + 20% of alcohol, 1·32 g. of colourless prisms, m. p. 144·5—145°, were obtained. The pure acid had hitherto not been obtained. *p*-Nitrobenzoyl cyanide, when similarly treated with hydrochloric acid, yields, not *p*-nitrophenylglyoxylic acid, but pure *p*-nitrobenzoic acid.

(b) Phenylbromocyanonitromethane (0·34 g.) in 5 c.c. of concentrated sulphuric acid was red at first and changed within 5 minutes through deep purple to deep blue, in another 15 minutes to greenish-blue, in another 20 to deep green, in a further 50 minutes to deep brown. 0·502 G. of phenylbromocyanonitromethane in 5 c.c. of concentrated sulphuric acid gave after a few hours a distinct test for benzoyl cyanide (odour on diluting a few drops of the solution); after 22 hours, 0·271 g., m. p. 60—65°, was extracted by ether from the solution, poured on ice. 1·017 G. of phenylbromocyanonitromethane in 8 c.c. of concentrated sulphuric acid was left for 18 days, and water was then slowly added without cooling (gas evolution). Filtration of the cold liquid left 0·441 g. of benzoic acid (m. p. 105—110°; mixed m. p.) and extraction of the filtrate with ether gave 0·111 g. of less pure benzoic acid (m. p. 95—102°). Since, on similar treatment, some benzoic acid (m. p. 112—114°) was obtained from the above product of m. p. 60—65°, the latter consisted, no doubt, essentially of phenylglyoxylic acid (m. p. 65—66°).

(c) The sodium salt of phenylcyano*iso*nitromethane (0·5 g.) in 5 c.c. of concentrated sulphuric acid gave at once a bright blue colour, changing within 5 minutes to purple, blue-green, green and olive-green, and within an hour to brown. On pouring the liquid into water after 48 hours and extracting the solution with ether, 0·312 g. of a dark brown, oily substance was obtained which, by sublimation at 90—100°, gave impure benzoic acid (m. p. 93—105°; mixed m. p.).

11. *Reactions of ethyl phenylbromomalonate.* This was prepared according to Wheeler and Johnson (*J. Amer. Chem. Soc.*, 1902, **24**, 688) and distilled at 135—136° (2 mm.) (Found: Br, 25·2. Calc. for $C_{13}H_{15}O_4Br$: Br, 25·4%).

(a) Potassium iodide test: 0·309 g. of the ester in 20 c.c. of benzene was mechanically shaken with 2 g. of potassiun iodide in 20 c.c. of water for 45 minutes. A mere trace of iodine was liberated, the colour developed with starch being discharged by a single drop of N/10-thiosulphate.

(b) Ammonia test: 0·691 g. of the ester, dissolved in 60 c.c. of dry petrol (b. p. 30—50°), was treated with dry ammonia during 22 minutes. An immediate slight unfilterable opalescence was produced, but no further change. After the solution had been shaken with dilute aqueous ammonia, the latter gave a very slight positive bromine test.

(c) Aniline test: 1·055 g. of the ester were heated at about 95°, for 2 hours, with 3·165 g. of aniline in an atmosphere of carbon dioxide. The product was shaken with 100 c.c. of cold 5% nitric acid and the solution obtained was freed from insoluble semi-oil by means of benzene and treated with silver nitrate, 0·1958 g. of silver bromide, corresponding to 31·2 mol.% of hydrogen bromide, being precipitated. The filtrate was made alkaline with ammonia and shaken with ether, and the extract was washed once with water and evaporated. The residue contained 0·47% of bromine (Carius), corresponding to approximately 5·3 mol.% of bromoaniline, calculated on the ester used.

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LXIII.—*The Alkylation of α-Cyano-β-alkylacrylic Esters and of α-Phenyl-β-alkylacrylonitriles.*

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ETHYL *cyclo*hexylidenecyanoacetate (I) (Harding, Haworth, and Perkin, J., 1908, **93**, 1956; Lapworth and McRae, J., 1922, **121**, 2741) readily reacts with phenacyl bromide or methyl iodide in presence of sodium ethoxide, giving derivatives of type (II).

$$\text{(I.)}\quad CH_2{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}C{:}\underset{CO_2Et}{C}\cdot CN \qquad CH_2{<}{}^{CH_2\cdot CH_2}_{CH_2-CH}{\gg}C\cdot\underset{CO_2Et}{CR}\cdot CN\quad\text{(II.)}$$

$$\text{(III.)}\quad C_5H_{11}\cdot CH_2\cdot CH{:}C(CN)\cdot CO_2Et$$

This was thought by the former authors to furnish fairly conclusive evidence of the validity of structure (II; R = H) which they assigned to the substance, but the products of decomposition were shown by the latter authors to support the formula (I). Other reactions of this ester were found to be in agreement with this structure and it was pointed out that the formation of alkyl derivatives (II) can be explained on the basis of the structure (I). Strong evidence has been presented by Harding, Haworth, and Perkin for the methyl derivative of ethyl *cyclo*hexylidenecyanoacetate having a structure of type (II), but since a search of the literature disclosed that these seemed to be the only genuine cases of unsaturated α-cyano-esters having the double bond in the βγ-position, it seemed to us desirable to investigate such derivatives of α-cyano-β-alkylacrylic esters by the methods used by Lapworth and McRae in their study of ethyl *cyclo*hexylidenecyanoacetate and ethyl heptylidenecyanoacetate (III) in order to establish conclusively the structure (II) as that of these alkyl derivatives and at the same time to ascertain the behaviour of these substances towards those reagents with which the parent αβ-unsaturated substances give characteristic results.

This has now been done with the *n*-butyl and ethyl derivatives of ethyl *cyclo*hexylidenecyanoacetate and with the *n*-butyl derivative (IV) of ethyl heptylidenecyanoacetate. It was also our intention to prepare and examine in the same way derivatives of

$$\underset{\text{(IV.)}}{C_5H_{11}\cdot CH{:}CH\cdot C(C_4H_9)(CN)\cdot CO_2Et} \qquad \underset{\text{(V.)}}{CH_2{<}{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}C{:}CPh\cdot CN}$$

$$\text{(VI.)}\quad C_5H_{11}\cdot CH_2\cdot CH{:}CPh\cdot CN$$

the similarly constituted α-phenyl-β-alkylacrylonitriles, but in repeated attempts we failed to obtain any evidence that either

*cyclo*hexylidenephenylacetonitrile (V) or α-phenyl-β-hexylacrylonitrile (VI) forms alkyl derivatives.

Ozone is rapidly absorbed by the above-mentioned three alkyl derivatives and the decomposition of their ozonides leads precisely to those products to be expected from formulæ (II) and (IV); namely, in the case of *ethyl* α-n-*butyl*-Δ^1-cyclo*hexenylcyanoacetate*, ethyl *n*-butylcyanoacetate and adipic acid; from the ozonide of the corresponding *ethyl* derivative, only adipic acid was isolated; and from the ozonide of *ethyl α-cyano-α-*n*-butyl-Δ^β-nonenoate* (IV), the substances isolated were hexaldehyde, formic acid, and *n*-butylmalonic acid. The behaviour of these alkyl derivatives in absorbing bromine instantly and in giving no reaction with either potassium cyanide or sodium bisulphite is in accord with their βγ-unsaturation and is in such marked contrast with the behaviour of the parent esters towards these reagents that it must be concluded that only the merest trace of the βγ-isomeride can be present in ethyl *cyclo*hexylidenecyanoacetate and that these two forms do not present a case of tautomeric equilibrium in which the position of equilibrium is quickly restored if disturbed.

The ozonisation results outlined above dispose of the suggestion of Lapworth and McRae that the sodio-derivatives might have *inter alia* the structure R′·CNaR″·CR‴:C(CN)·CO_2Et. The preparation of the *n*-butyl derivative of ethyl heptylidenecyanoacetate supplements the results of Lapworth and McRae, who failed to obtain benzyl and phenacyl derivatives of this substance in a state pure enough for characterisation, although reactions with benzyl chloride and phenacyl bromide in the presence of sodium ethoxide occurred readily. Their statement of these results has been misinterpreted by Birch, Kon, and Norris (J., 1923, **123**, 1361) to mean that no alkylation had taken place and a "ready interpretation," now obviated, of this supposed failure to form alkyl derivatives was advanced. The latter authors are of the opinion that to form these alkyl derivatives the βγ-phase of the αβ-unsaturated α-cyano-ester is necessary and it was concluded that this was absent or suppressed in ethyl heptylidenecyanoacetate through a tendency to form a doubly conjugated system. If it be granted that such isomeric change is a necessary preliminary to alkylation, then it can take place apparently with almost equal facility in both ethyl *cyclo*hexylidenecyanoacetate and ethyl heptylidenecyanoacetate.

During the course of our attempts to alkylate *cyclo*hexylidenephenylacetonitrile we obtained further evidence in support of Birch and Kon's contention (J., 1923, **123**, 2440) that this substance should have the constitution (V) rather than the βγ-structure (VII) of Harding and Haworth (J., 1910, **97**, 486), in that it readily

combines with hydrogen cyanide, forming 1-*cyanocyclohexylphenylacetonitrile* (VIII).

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\gg C\cdot CHPh\cdot CN \quad CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(CN)\cdot CHPh\cdot CN$$

(VII.) (VIII.)

(IX.) $C_6H_{13}\cdot CH(CO_2H)\cdot CHPh\cdot CO_2H$

Heptaldehyde has now been condensed with phenylacetonitrile, giving *α-phenyl-β-n-hexylacrylonitrile* (VI); this combines with hydrogen cyanide to form a dinitrile, which was not isolated but was hydrolysed to *α-phenyl-α′-n-hexylsuccinic acid* (IX).

EXPERIMENTAL.

Ethyl α-n-Butyl-Δ¹-cyclohexenylcyanoacetate (II; $R = C_4H_9$).—The sodio-derivative of ethyl *cyclo*hexylidenecyanoacetate prepared from 19·3 g. of the ester and 2·3 g. of sodium in 50 c.c. of absolute alcohol was heated under reflux on a steam-bath for 2 hours with *n*-butyl iodide (23 g.). Water and ether were then added; the ethereal solution was washed with sodium carbonate solution and dried with calcium chloride. After evaporation of the ether the residue was fractionated under reduced pressure; the fraction, b. p. 162—165°/15 mm., on redistillation, yielded 15 g. of the pure *ester*, b. p. 163—164°/15 mm. (Found: C, 72·1; H, 9·4; N, 5·7. $C_{15}H_{23}O_2N$ requires C, 72·3; H, 9·2; N, 5·6%). The pure ester absorbed bromine readily, but eventually hydrogen bromide was liberated, pointing to a certain amount of substitution. Attempts to effect the addition of hydrogen cyanide gave only the unchanged ester.

Ethyl α-Ethyl-Δ¹-cyclohexenylcyanoacetate (II; R = Et).—The preparation of this derivative was carried out precisely as described above, except that ethyl iodide (30 g.) was substituted for the *n*-butyl iodide. After three distillations, 10 g. of the pure *ester*, b. p. 168°/22 mm., were obtained (Found: C, 70·1; H, 8·5; N, 6·7. $C_{13}H_{19}O_2N$ requires C, 70·6; H, 8·6; N, 6·3%). Its behaviour with bromine and with potassium cyanide is exactly parallel to that of the butyl derivative.

Ozonisation of Ethyl α-n-Butyl-Δ¹-cyclohexenylcyanoacetate.—A solution of 10 g. of the ester in chloroform was treated with a stream of ozonised oxygen for 15 hours; no further absorption of ozone then seemed to take place. The thick, syrupy residue remaining after removal of the chloroform under reduced pressure was warmed on a steam-bath for 30 minutes with 25 c.c. of 6% sulphuric acid and 3 g. of potassium ferrocyanide. The resulting solution was repeatedly extracted with ether. After being washed several times

with sodium bicarbonate solution (A), the combined ethereal extracts were evaporated and the residue was treated again with sulphuric acid and potassium ferrocyanide, ultimately giving another extract (A) and an ethereal solution, which on evaporation yielded an oil (B).

The sodium bicarbonate extract (A) was acidified and extracted with ten successive portions of ether, which were united, washed once with a little water, and evaporated. The oily residue, which readily crystallised, reduced ammoniacal silver nitrate, but did not affect Fehling's solution—properties in accord with those given by Harries (*Ber.*, 1908, **41**, 3557) for the half-aldehyde of adipic acid. It was evaporated to dryness on the water-bath with nitric acid; the residue, after one crystallisation from acetone, yielded 3 g. of adipic acid, identified by melting point (149°) and by comparison with a genuine specimen (Equiv.: found, 73·1; calc., 73·1).

The oily residue (B) was distilled under reduced pressure and two fractions were collected: (i) up to 130°/15 mm. (3·8 g.), (ii) 130—210°/15 mm. (3·8 g.). The first fraction on hydrolysis with alcoholic potash evolved much ammonia. After removal of the alcohol, the solution was acidified and repeatedly extracted with ether. The ethereal extract on evaporation yielded 3·2 g. of an acid which, after recrystallisation from acetone, melted at 102—103°, alone or mixed with a genuine specimen of *n*-butylmalonic acid (Equiv.: found, 80·1; calc., 80·0). The formation of this acid and the production of ammonia establish the fact that ethyl *n*-butylcyanoacetate is one of the original products of the decomposition of the ozonide.

The second fraction, of which the greater portion distilled at 195°/15 mm., deposited a crystalline acid on cooling, which was separated from the oil by repeated extraction with water. The combined extracts on evaporation yielded 1·4 g. of pure adipic acid. The oil on hydrolysis with alcoholic potash yielded a further 1·9 g. of *n*-butylmalonic acid. The recovery of adipic acid (4·4 g.) and of *n*-butylmalonic acid (5·1 g.) was respectively 77 and 79% of that theoretically possible.

Ozonisation of Ethyl α-Ethyl-Δ^1-cyclohexenylcyanoacetate.—Two g. of the ester, subjected to the action of ozone as described in the case of the *n*-butyl derivative, yielded 0·6 g. of pure adipic acid. There was insufficient neutral ester to make a search for ethylmalonic acid feasible.

Ethyl α-Cyano-α-n-butyl-Δ^β-nonenoate (IV).—The ester (III) required for this preparation was prepared by a modification of Lapworth and McRae's method (*loc. cit.*). A mixture of 57 g. of

ethyl cyanoacetate and 1 g. of piperidine is cooled in salt and ice, and 57 g. of heptaldehyde are added at such a rate that the temperature remains below 0°. The mixture is kept in ice for 24 hours and then treated in the usual way. The yield of pure ester, boiling at 152—154°/13 mm. rather than at 144—145°/13 mm. as previously recorded, is 80—84 g.

Alkylation was effected by adding 23 g. of *n*-butyl iodide to the sodio-derivative prepared by adding 22 g. of the ester (IV) to a cooled solution of 2·3 g. of sodium in 50 c.c. of absolute alcohol, and warming the mixture gently on a water-bath for 90 minutes. The mixture was then poured into a large volume of dilute acid and extracted with ether, and the extract was washed successively with dilute sodium carbonate solution and with water. After the ethereal solution had been dried and evaporated, the residue was fractionated under reduced pressure. By combining the fractions, b. p. 160—180°/17 mm., from several operations and redistilling them, the pure *ester*, b. p. 154—156°/11 mm., was obtained (yield, 10%) (*Found*: C, 72·4; H, 10·0; N, 5·7. $C_{16}H_{27}O_2N$ *requires* C, 72·5; H, 10·2; N, 5·3%). The sodium carbonate extract mentioned above gave 6 g. of a strongly acid substance on acidification. A pure substance has not been isolated from it. The ester readily absorbs bromine in carbon tetrachloride solution, and hydrogen bromide is liberated in appreciable quantity only on prolonged treatment. A pure dibromo-derivative was not isolated.

*Ozonisation of Ethyl α-Cyano-α-*n*-butyl-Δ^{β}-nonenoate* (IV).—After a stream of ozonised oxygen had been passed into 6 g. of the pure ester for 35 hours, the material was heated on a water-bath for 1 hour with 50 c.c. of 4% sulphuric acid and then steam-distilled until 50 c.c. of distillate had been collected, leaving an oily mixture in the distilling flask (A). The distillate was shaken with sodium bisulphite, and an oil which remained undissolved was extracted with ether (B). The aqueous bisulphite solution was made alkaline with sodium carbonate and distilled in steam. The distillate was shaken with an excess of semicarbazide hydrochloride and sodium acetate. A solid semicarbazone separated which was filtered off and cautiously washed with ether. The melting point of this product (0·5 g.), alone or mixed with a genuine specimen of hexaldehyde semicarbazone, was 106°. Admixture with an equal weight of the semicarbazone of heptaldehyde (m. p. 106°) caused a depression of over 6°. Recrystallisation from methyl alcohol did not change the melting point.

The ethereal solution containing the oil (B) was evaporated, and the residue heated with alcoholic potash until evolution of ammonia

ased. The acidified solution was repeatedly extracted with her. The ethereal solution on evaporation left a thick oil, from hich 0·1 g. of an acid, m. p. 89°, crystallised in several days. On eating to a higher temperature, a gas, probably carbon dioxide, as evolved. The crude acid yielded an equivalent of 85 (*n*-butylalonic acid requires equiv. 80·0). When calcium chloride solution as added to a neutral solution of the sodium salt, a crystalline lcium salt was precipitated. Although insufficient acid was btained to identify it further, the authors regard this as slightly npure *n*-butylmalonic acid.

Examination of the oil (*A*). *Isolation of* n-*butylmalonic acid.* he oil was extracted with ether, and then hydrolysed with alcoholic otash, ammonia being evolved in considerable quantity. From ie product of hydrolysis, 0·6 g. of *n*-butylmalonic acid was isolated s described above and identified by its melting point, 102°, and s equivalent (Found, 81).

Examination of the aqueous solution remaining in the distillation ask. Detection of formic acid. The aqueous solution was heated) expel the ether and distilled until only a small volume remained. he distillate (150 c.c.) was strongly acid and gave the following ests for formic acid: (*a*) The odour of ethyl formate on esterifiction; (*b*) reduction of mercuric chloride to mercurous chloride nd of silver nitrate to metallic silver; (*c*) reduction with magnesium powder yielded an appreciable quantity of formaldehyde.

Experiments with cyclo*Hexylidenephenylacetonitrile* (V).—Birch and Kon (J., 1923, **123**, 2446) mention that this nitrile is somewhat difficult to purify. If, however, the substance prepared by Harding and Haworth's method (J., 1910, **97**, 497) is carefully fractionated under reduced pressure, it solidifies, on cooling, to a colourless, crystalline mass, which, after being drained on tile and cautiously washed with ether, melts at 28° and boils at 176—178°/12 mm. Piperidine does not effect the condensation of *cyclo*hexanone with phenylacetonitrile.

The nitrile (19·7 g.) was added to sodium ethoxide made from 2·3 g. of sodium and 40 c.c. of absolute alcohol. The yellow solution was heated under reflux for 3½ hours with 21 g. of *n*-butyl iodide, the neutral mixture poured into water, and the oil extracted with ether. The residue obtained from the dried evaporated extract gave 17·3 g. of an oil, b. p. 178—180°/13 mm., which solidified almost completely when cooled and seeded with *cyclo*hexylidenephenylacetonitrile. A portion pressed on tile and cautiously washed with alcohol melted at 28°, alone or mixed with the original nitrile (Found: C, 85·5; H, 7·8; N, 7·1. Calc.: C, 85·3; H, 7·6; N, 7·1%).

The above procedure was varied by using *n*-butyl bromide, ethyl bromide, and also a large excess of sodium ethoxide, but the unchanged nitrile was recovered almost quantitatively. The alkyl halide was always used up, even in the cold, whereas in the absence of the nitrile reaction is very slow.

A mixture of 19·7 g. of the nitrile (V), 13 g. of potassium cyanide, 20 c.c. of water, and 100 c.c. of alcohol was gently heated on a water-bath for 5 hours. The resulting brown mixture was poured into a litre of boiling, very dilute sodium hydroxide solution, and boiling continued for 20 minutes. The separated oil, which readily crystallised, was filtered off (yield, 18 g.), washed, and recrystallised twice from alcohol. It softened at 258° and began to decompose above 264° (Found : C, 80·4; H, 7·3; N, 12·2. $C_{15}H_{16}N_2$ requires C, 80·5; H, 7·1; N, 12·5%). Partial hydrolysis of the 1-*cyano*cyclo*hexylphenylacetonitrile* (VIII) could be effected by heating on the steam-bath for 10 hours with 90% sulphuric acid. No charring occurred and the mixture of amide and imide on further hydrolysis with potash yielded an acid which was difficult to purify.

*α-Phenyl-β-*n*-hexylacrylonitrile* (VI).—Owing to the ease with which heptaldehyde polymerises, special precautions must be observed in this preparation, especially since piperidine does not effect the condensation. Heptaldehyde (30 g.) was slowly added to a solution, cooled to − 10°, prepared by adding 40 g. of phenylacetonitrile to a solution of 6·1 g. of sodium in 200 c.c. of absolute alcohol. The mixture was left in a freezing mixture for 6 hours, allowed to come to room temperature over-night, and then poured into dilute acid. The oil was extracted with ether, washed with sodium carbonate solution, and dried. The residue obtained after removal of the ether gave 41 g. of a fraction, b. p. 162—173°/13 mm., which after two distillations gave the pure *nitrile*, b. p. 168—170°/13 mm. (Found : C, 84·6; H, 9·0; N, 6·7. $C_{15}H_{19}N$ requires C, 84·5; H, 8·9; N, 6·6%).

Attempts to add on the elements of hydrogen cyanide with subsequent hydrolysis gave in one case a product which seemed to consist largely of *α-phenyl-α′-*n*-hexylsuccinic acid* (IX). In another experiment an acid, m. p. 170°, equiv. 270, was obtained ($C_{16}H_{22}O_4$ requires equiv., 278). The results show that although undoubtedly hydrogen cyanide is added on, the primary process of the reaction is very slow, giving opportunity for the occurrence of secondary reactions (compare Lapworth and McRae, *loc. cit.*, p. 2747). In view of the uncertainty the authors deem it unnecessary to enter into experimental details.

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LXIV.—*On Haber's Glass Cell.*

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SEVERAL workers (Hughes, *J. Amer. Chem. Soc.*, 1922, **44**, 2860; Kerridge, *Biochem. J.*, 1925, **19**, 611) have found that the glass cell described by Haber (*Z. physikal. Chem.*, 1909, **67**, 385) can be used to measure hydrogen-ion concentration under conditions which render the hydrogen electrode useless, as in the presence of strong oxidising agents; but difficulties sometimes arise in its use.

The purposes of this paper are (1) to discuss certain factors affecting the behaviour of Haber's cell, and the technique of making and using it; (2) to give experimental data explaining the mechanism by which the cell functions; (3) to show some results obtained by using the cell in various solutions the hydrogen-ion activity of which cannot be readily measured with the hydrogen electrode.

I. *Preparation of Bulbs; Effect of Composition of Glass.*

The chief difficulty in the use of Haber's cell is that it does not readily give reproducible results. There are several reasons for this difficulty. As Mrs. Kerridge (*loc. cit.*) has shown, there is always an asymmetry *E.M.F.* between the two sides of a glass membrane in contact with the same electrolyte which may take several days to become constant. This asymmetry varies even in different cells made from the same glass. It has also been found in almost every case that the change in *E.M.F.* of the glass cell corresponding to a given change in p_H of the solution in contact with the bulb varies from cell to cell, and from day to day in the same cell.

Mrs. Kerridge recommends checking all p_H measurements with the glass cell by measuring the *E.M.F.* of the cell when filled with a standard buffer mixture. It is still better to check the measurement of p_H in the solution under examination by measuring the *E.M.F.* produced by two standard buffer mixtures, one slightly more and the other slightly less acid than the solution; the required p_H can then be interpolated, and errors due to both the above-mentioned sources will be eliminated.

Mrs. Kerridge also suggests the use of very thin bulbs, which not only conduct better and reach a constant asymmetry *E.M.F.* sooner, but give a greater change in *E.M.F.* for a given change in p_H.

In one of our experiments on the effect of bulb thickness, a thin bulb gave a change of 0·514 volt when transferred from *N*/1-hydrochloric acid to a *M*/40-sodium diborate solution of about p_H 9·2. A thick bulb only changed its *E.M.F.* by 0·300 volt under the same conditions. Moreover, it is important to blow the bulbs as rapidly as possible, for prolonged or repeated heating of the bulb, especially if devitrification sets in, may spoil it.*

The composition of the glass has an important influence on the behaviour of Haber's cell. Most workers recommend "soft soda-lime glass," but different samples of such glass vary enormously in their suitability for this purpose, for which the glass should have a high conductivity; should rapidly reach a constant asymmetry *E.M.F.*; should give as nearly as possible the same change in *E.M.F.*, ΔE_g, as the hydrogen cell, ΔE_h, for a given change in p_H; and should change its *E.M.F.* as little as possihle on standing in alkaline solutions. These properties were studied in several samples of glass of known composition. The results are in Table I.

Several other samples of ordinary soft glass tubing were found to vary in their suitability for glass electrodes; none was better than 793A, which was furnished by the Department of Glass Technology, Sheffield University. The less alumina a glass contains the better it is for glass-cell work; also a high soda content tends to increase the conductivity of the glass, whereas potash seems to decrease it.

Sample 793A had such a high conductivity that no electrostatic shielding whatever was necessary. In addition to the above-mentioned qualities, this sample had the important property of being almost unaffected by large changes in sodium-ion concentration, provided the hydrogen-ion concentration is not less than 10^{-9} (see Section II). Some of the samples of glass tested by Mrs. Kerridge (*loc. cit.*) were somewhat affected by the sodium-ion concentration.

After the above experiments on the effect of composition were completed, another sample of glass was found which was very nearly as good as 793A as regards conductivity and the closeness with which it followed the hydrogen electrode. It had the additional advantages

* Rebbeck and Ferguson (*J. Amer. Chem. Soc.*, 1924, **46**, 1991) found that annealing glass reduced its conductivity and drove off the surface layers of absorbed water, both of which effects would be detrimental to its usefulness as a Haber electrode. Further, Dr. E. C. Smith (unpublished communication) found that heating a glass bulb in an autoclave destroyed its hydrogen-electrode function completely.

TABLE I.

Composition and properties of various glasses.

	No. 1; X-ray.	No. 2; soft German glass.	No. 3; Moncrieff.	No. 793A.	No. 444.
SiO_2	66·88%	70·62%	67·56%	71·83%	72·19%
Al_2O_3	4·60	3·23	6·53	0·44	8·96
TiO_2	Trace	Trace	Trace	—	—
Fe_2O_3	0·08	0·11	0·13	0·04	—
MnO	Trace	Trace	0·17	—	—
CaO	6·76	7·58	6·54	8·36	0·08
MgO	0·81	0·25	—	Trace	—
Na_2O	15·48	15·48	15·62	18·83	18·79
K_2O	5·56	2·62	3·34	—	—
SO_3	—	—	—	0·22	—
Total	100·17	99·89	100·09	99·72	100·02
Conductivity.	Very low; hence sample useless.	Good.	Poor.	Excellent.	Good.
$\Delta E_g/\Delta E_h$ (over range p_H 0—10).	—	0·92	0·88	0·95—0·98	0·24—0·27 (very variable)
Asymmetry.	—	High; slow *in attaining* constancy.	Very high; slow in attaining constancy.	Very low; attains constancy in a few hours.	Fairly low; attains constancy in a few hours.
Decrease in *E.M.F.* on standing in *N*-KOH over-night.	—	*0·010—0·090*	*0·077—0·090*	*0·005—0·070*	*0·121* [in 0·3*N*-$Ba(OH)_2$ sol.]; *E.M.F.* variable even in acid solution.

of being more easily workable and of being commercially obtainable, being supplied as "white flint" glass by Wood Bros. Glass Co., Barnsley, Yorks. Analysis: SiO_2, 69·75; Sb_2O_3, 0·22; Fe_2O_3, 0·05; Al_2O_3, 1·04; MnO, 0·21; CaO, 11·26; MgO, trace; Na_2O, 16·54; K_2O, 0·66; SO_3, 0·34%. Total, 100·07.

The form of glass cell used in the following experiments (see Fig. 1) was a modification of Haber's cell. The bulb was filled with *N*-hydrochloric acid; the inside electrode consisted of a drop of mercury covered with calomel, touching a platinum wire sealed through a glass tube. Above the seal was another drop of mercury with the lead-in wire dipping into it. This electrode could be kept at the temperature of the liquid surrounding it which was contained in a beaker immersed in a paraffin-oil thermostat. The neck of the bulb was held in a paraffin-wax-coated block of wood cut to fit the beaker as a cover, and the rim of the beaker was supported by the paraffin-wax-coated wooden thermostat cover.

The little mercury–calomel–hydrochloric acid electrode could be transferred from the inside of the bulb to the outside when the beaker was filled with *N*-hydrochloric acid in order to measure the asymmetry *E.M.F.* of the bulb.

The external electrode was a saturated potassium chloride–calomel half cell, contained in a tube submerged in the bath as shown in Fig. 2.

The electrometer was of the Compton type, made by the Cambridge Instrument Co., giving a deflexion of about 1·5 mm. at 1 m.

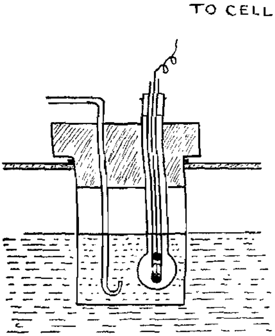


FIG. 1.

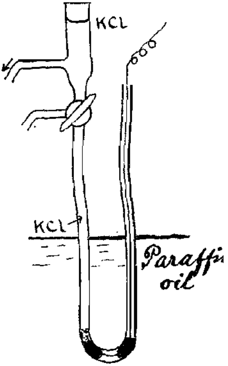


FIG. 2.

per millivolt with the vane charged ±50 volts with respect to earth. It was used as a null instrument in the usual way. The wiring

FIG. 3.

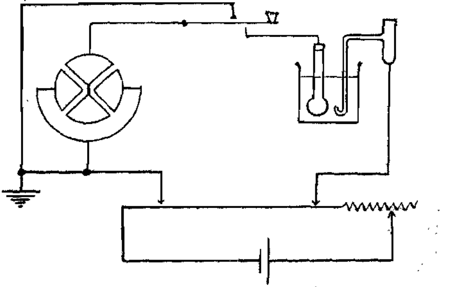


diagram is shown in Fig. 3. Connexion was made from the unearthed quadrants to the inside electrode of the glass cell by means of a two-way tapping key mounted on a vulcanite block. When

the key was released both sets of quadrants were earthed. The key could be dismounted so that the vulcanite base could readily be cleaned to remove conducting surface films of moisture.

II. *Mechanism of the Hydrogen-electrode Function in Haber's Glass Cell.*

Influence of Certain Ions other than Hydrogen.—Horovitz (*Z. Physik*, 1923, **15**, 369) and Schiller (*Ann. Physik*, 1924, **74**, 105) showed that the potential of Haber's glass cell might be a function, not only of hydrogen-ion concentration, but also of other ionic concentrations in the solution in contact with the glass. If the bulb was made of a glass containing much boric oxide, the sodium ion had as much effect as the hydrogen ion on the *E.M.F.* of the cell. They think that glass functions as an electrode by virtue either of (1) its composition as a solid electrolyte, or of (2) an exchange between cations in the surface of the glass and cations from the solution. Thus the sodium-electrode function of the sodium borosilicate glasses is due to their sodium content, whilst the hydrogen-electrode function of soda–lime glass is due to hydrogen ions from the solutions which have replaced other ions in the surface of the glass.

Freundlich and Rona (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, 396) showed that the electrokinetic potential of glass, which was greatly influenced by the surface adsorption of polyvalent ions, had very little connexion with the Haber potential. Schiller must have assumed that ionic exchange may affect the deeper layers of the glass, thus influencing the Haber potential as well as the electrokinetic potential.

This theory does not give an adequate explanation of how the hydrogen-ion concentration in the glass phase is maintained relatively constant when that of the solution changes. The following experiment illustrates the point: A fresh-blown bulb of No. 793A glass was filled with *N*-hydrochloric acid, and allowed to stand a few hours so that the inner surface could come to equilibrium. The electrode within the bulb was mercury and calomel in contact with the acid. The bulb was then dipped in *N*-potassium hydroxide, the outside electrode being a saturated potassium chloride calomel half cell. The *E.M.F.* of the cell, measured immediately at 15°, was 0·624 volt (outside positive), remaining constant for 20 minutes. The bulb was then transferred to a *N*-hydrochloric acid solution, and the *E.M.F.* was then 0·028 volt (outside negative). The change in the *E.M.F.* of the glass cell was thus 0·652 volt. The corresponding change for the hydrogen cell would be about 0·783 volt. This difference of 0·131 volt corresponds to a change

of about 196 to 1 in the hydrogen-ion concentration of the glass (assuming the glass to be functioning only as a hydrogen electrode), *i.e.*, glass in contact with *N*-hydrochloric acid has only 196 times the hydrogen-ion concentration of glass in contact with *N*-potassium hydroxide, although the ratio of the hydrogen-ion concentrations of the solutions is about 5×10^{13}. If the hydrogen ions in the glass phase were derived solely by ionic exchange from the solutions in contact with the glass, one would expect a far greater difference in the hydrogen-ion concentration in the glass.

It is easier to suppose (as Haber did) that the hydrogen ions in the glass phase are derived from water from the solution which dissolves in the glass. Frazer, Patrick, and Smith (*J. Physical Chem.*, 1927, **31**, 897) have recently demonstrated that a considerable amount of water is adsorbed by glass in contact with acids.

Our experimental results are best explained on the view that the hydrogen-ion concentration in the glass phase is held relatively constant by the buffer action of the glass which is a mixture of the salt of a weak acid (Na_2SiO_3) with the anhydride of that acid (excess SiO_2). This action *prevents* ionic exchange between the glass phase and the solution from altering the hydrogen-ion concentration in the glass, which is thus maintained relatively constant in spite of the exchange of ions with the solution. The effect of ions other than hydrogen on the *E.M.F.* of sample 793A was negligible except in alkaline solutions. In solutions containing sodium or lithium hydroxide the decrease in log $[H^+]$ in the glass becomes greater than its decrease in the solution as the concentration of the base is increased beyond *N*/10. This effect is shown in the following experiments :

Glass : No. 793A ; temp. : 25° ; cell : Hg|HgCl|KCl (satd.)|solution|glass| *N*-HCl|HgCl|Hg.

Solution.	*E.M.F.* of cell.	Solution.	*E.M.F.* of cell.
N/100-NaOH	0·645	*N*/100-LiOH	0·660
N/10- ,,	0·681	*N*/10- ,,	0·704
N/1- ,,	0·678	*N*- ,,	0·699
10*N*- ,,	0·588	3·3*N*- ,,	0·677 decreasing to 0·662.

The effect of increasing concentrations of caustic soda was explained by Horovitz and Schiller as being due to the sodium-electrode function of the glass; this might be true in those cells which have a sodium-electrode function even in acid solution, but in the above case the glass showed no indication of such a function in any solution more acid than p_H 9. Furthermore, the lithium ion produces the same effect and the glass (having no lithium ions initially, nor any means of maintaining a constant lithium-ion

concentration within itself if lithium ions penetrate from the solution) could hardly act as a lithium electrode. The reason why log [H^+] of the glass phase decreases more rapidly than that of the solution when the concentration of hydroxide exceeds $N/10$ is that in this region the buffer action of the glass breaks down and its surface is rapidly attacked and dissolved.

The effect of alkaline solutions in increasing the divergence between the *E.M.F.* of the glass and of the H_2|Pt begins to be noticeable at about p_H 9, *i.e.*, at the point where the buffer action of the sodium hydrogen silicate in the glass would begin to resist the action of alkaline solutions less effectively, since the apparent first dissociation constant of H_2SiO_3 is about 10^{-9} (Hägg, *Z. anorg. Chem.*, 1926, **155**, 21). The rapidly increasing divergence between the two *E.M.F.*'s in the presence of sodium and lithium ions begins at about p_H 13, and the apparent second dissociation constant of H_2SiO_3 is 10^{-13} (Hägg, *loc. cit.*). Beyond this p_H it is probable that the surface of the glass is attacked with greatly increasing rapidity as the solution becomes more alkaline. The difference in the action of the various hydroxides is probably due to a greater power of penetrating the glass possessed by the lithium ions, and is shown in the following experiments, from which it will be seen that the behaviour of different cells may not be the same.

	Glass, 793A.				*Another bulb, same glass.*		
Solution.	Glass cell *E.M.F.*	H_2|Pt *E.M.F.*	Diff.	Solution.	Glass cell *E.M.F.*	H_2|Pt *E.M.F.*	Diff.
N-HCl	−0·026	0·248	0·274	*N*-HCl	−0·024	0·248	0·272
N-KOH	+0·707	1·056	0·349	*N*-KOH	+0·767	1·055	0·288
N-NaOH	+0·669	1·045	0·376	*N*-NaOH	+0·675	1·044	0·369
N-LiOH	+0·617	1·041	0·424	*N*-LiOH	+0·420	1·040	0·620

Another fact indicating that the effect of sodium and lithium ions in strongly alkaline solution is due to a decrease in hydrogen-ion concentration in the glass phase, rather than to a sodium- or lithium-electrode function of the glass, is that the *E.M.F.* of a glass cell falls with time on standing in alkaline solution, *i.e.*, with increasing penetration by sodium or lithium ions. Now if the glass were functioning chiefly as a sodium or lithium electrode, the *E.M.F.* would change in the opposite direction as the ions penetrated the glass.

Yet another indication that the glass is still acting, at least partly, as a hydrogen electrode even in alkaline solution is the slow reversibility of the sodium hydroxide effect, shown as follows: A glass electrode, having an *E.M.F.* of 0·572 volt in 10*N*-sodium hydroxide solution, was transferred to *N*-potassium hydroxide solution, and the *E.M.F.* measured immediately was 0·668 volt, whereas that

measured after 30 mins. was 0·698 volt. The *immediate rise after* transference might be attributed to the decrease of sodium-ion concentration in the solution, but if the glass had been functioning chiefly as a sodium electrode, the slow drift in *E.M.F.* after the transference would have been in the opposite direction, since the *sodium ions would become less concentrated in the glass* phase and more concentrated in the solution.

The only real case of an electrode function in glass produced by exchange of ions with the solution seems to be the silver-electrode function observed by Horovitz in glass which had stood over-night in contact with silver nitrate solution. It is possible that, if silver silicate has a low solubility product, the silver-ion concentration in the surface of the glass might remain sufficiently constant to account for Horovitz's results. No silver-electrode function could be produced in the samples now investigated. When a bulb had been left in contact with silver nitrate solution over-night it showed slight changes in *E.M.F.* on varying the silver-ion concentration (the p_H

TABLE II.

Influence of various cations other than H^+ on the *E.M.F.* of Haber's cell.

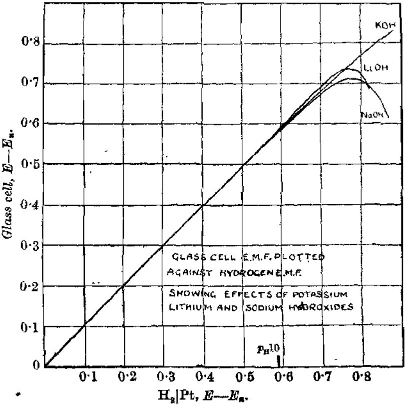
Temp. 25°. The sign of the *E.M.F.* is + or − according to whether the Hg|HgCl electrode is + or −.

Solution.	E_g.	E_h.	Diff.
Effect of K^+ ions.			
N-HCl	−0·019	+0·248	0·267
N-HCl satd. with KCl	−0·041	+0·223	0·264
KOH (app. 2*N*)	+0·660	+1·074	0·414
KOH (app. 2*N*) satd. with KCl	+0·673	+1·085	0·412
Effect of Na^+ ions.			
N-HCl	−0·023	+0·248	0·271
N-HCl satd. with NaCl	−0·066	+0·200	0·266
M/22-K_2HPO_4 + *M*/22-KH_2PO_4	+0·337	+0·640	0·303
M/22-K_2HPO_4 + *M*/22-KH_2PO_4 satd. with NaCl	+0·265	+0·568	0·303
M/20-$KH(BO_2)_2$	+0·470	+0·792	0·322
M/22-$KH(BO_2)_2$ satd. with NaCl	+0·420	+0·743	0·323
1·3*N*-KOH	+0·666	+1·061	0·395
1·3*N*-KOH satd. with NaCl	+0·560	+1·067	0·507
Effect of Li^+ ions.			
25 C.c. *N*-HCl	−0·030	+0·247	0·277
25 C.c. *N*-HCl + 25 g. LiCl	−0·121	+0·159	0·280
50 C.c. *N*-KOH	+0·756	+1·056	0·300
50 C.c. *N*-KOH + 10 g. LiCl	+0·692	+1·021	0·329
Same cell after 3 hrs.	+0·672	+1·021	0·349
Effect of Ca^+ ions.			
N-HCl	−0·026	+0·247	0·273
N-HCl + 20% $CaCl_2$	−0·043	+0·226	0·269
13% $CaCl_2$ soln. satd. with $Ca(OH)_2$	+0·540	+0·904	0·364
Dilute K_2CO_3 soln.	+0·520	+0·883	0·363

being maintained constant by very dilute sodium acetate–acetic acid buffer), but these *E.M.F.*'s varied considerably with time, and *rapidly approached the value for an ordinary bulb at the same* p_H.

In order to find to what extent the "mixed electrode functions" described by Horovitz and Schiller might exist in sample 793A, several comparisons were made between the *E.M.F.* of the glass cell and that of the hydrogen electrode before and after the addition of various salts (KCl, NaCl, $CaCl_2$, and LiCl): if the difference in *E.M.F.* remains unchanged after addition of a salt, the glass cell

FIG. 4.



must have a hydrogen-electrode function only. It is interesting to note (Table II) that the effect, if any, of adding potassium or sodium chloride on the difference in *E.M.F.* between the glass and hydrogen cells, is in the opposite direction to that which would be expected from Horovitz and Schiller's theory, when the solution is acid. Changes in the potassium-ion concentration affect the *E.M.F.* of the hydrogen electrode in the same way as they affect that of the glass cell; and similarly for sodium and lithium ions except in strongly alkaline solution. The calcium ion, however, has but little influence on the *E.M.F.* of the glass cell, even in alkaline solution.

The curves in Fig. 4 and data in Table III show the behaviour of the glass cell in the presence of potassium, lithium, and sodium

ions. The ordinates represent the difference between the E.M.F. of the glass cell filled with the solution which is being studied and that of the same cell filled with N-hydrochloric acid. The abscissæ represent the difference in E.M.F. of the hydrogen electrode when in the same solution as the glass electrode and when in N-hydrochloric acid. The glass was No. 793A; temperature 25°. Lithium and sodium hydroxides both show a maximum glass E.M.F. at about p_H *13. The difference between the effects of these ions on the glass cell becomes negligible when the hydrogen-ion activity is greater than* 10^{-10}.

The extent to which the glass cell *E.M.F.* departs from the value it would have if the glass had a perfect hydrogen-electrode function is measured by the difference between the abscissæ and ordinates of points on the curves.

TABLE III.

Data for curves (Fig. 4) showing relation between hydrogen and glass cell *E.M.F.* in solutions containing K˙, Na˙, and Li˙ ions.

Solution.	E_g.	$E_g—E_H$.	E_h.	$E_h—E_H$.
N-HCl	−0·025	0	0·247	0
N/10-HCl	+0·032	0·057	0·303	0·056
N/100-HCl.....................	+0·088	0·113	0·364	0·117
N/1000-HCl	+0·143	0·168	0·418	0·171
N/10,000-HCl	+0·196	0·221	0·472	0·225
N/1000-KOH	+0·576	0·601	0·860	0·613
N/100-KOH	+0·644	0·669	0·933	0·686
N/10-KOH	+0·702	0·727	0·997	0·750
N-KOH	+0·748	0·773	1·056	0·809
3*N*-KOH	+0·779	0·804	1·092	0·845
13*N*-KOH	+0·800	0·829	1·128	0·881
N-HCl	−0·026	0	0·247	0
0·1% $Na_2B_4O_7$	+0·484	0·510	0·770	0·523
N/1000-NaOH	+0·572	0·598	0·865	0·618
N/100NaOH	+0·645	0·670	0·941	0·694
N/10-NaOH	+0·681	0·706	0·998	0·751
N-NaOH	+0·678	0·703	1·050	0·803
10*N*-NaOH	+0·588	0·613	1·116	0·869
N-HCl	−0·024	0	0·247	0
0·02*M*-LiAc + 0·02*M*-HAc	+0·242	0·266	0·514	0·267
Li borate (about 0·02*M*) ...	+0·501	0·525	0·778	0·531
N/100-LiOH	+0·660	0·684	0·940	0·693
N/10-LiOH	+0·704	0·728	0·996	0·749
N-LiOH	+0·704—0·699	0·723	1·045	0·798
3·3*N*-LiOH	+0·677—0·662	0·686	1·066	0·819

III. *Applications of the Cell.*

The measurements of p_H by means of the glass cell (Table IV) show how it can be used in the presence of oxidising agents, of substances such as azoimide and hydrazine which poison a hydrogen electrode, and of a strongly coloured solution such as permanganic acid which precludes the use of indicator methods.

TABLE IV.

Glass, sample 793A. Temp., 25°.

Cell: Hg|HgCl|sat. KCl|*solution*|*glass*|*N*-HCl|HgCl|Hg.

Solution.	E_g.	p_H (apprx.).	Solution.	E_g.	p_H (apprx.).
$M/40$-$\begin{Bmatrix} KH_2PO_4 \\ K_2HPO_4 \end{Bmatrix}$ ...	0·360	6·79*	$M/10$-$\begin{Bmatrix} KC_2H_3O_2 \\ HC_2H_3O_2 \end{Bmatrix}$	0·241	4·63*
$M/40$-$\begin{Bmatrix} KH_2AsO_4 \\ K_2HAsO_4 \end{Bmatrix}$ ...	0·355	6·70	$M/10$-$\begin{Bmatrix} KN_3 \\ HN_3 \end{Bmatrix}$	0·233	4·49
$\begin{Bmatrix} M/40\text{-}K_2CrO_4 \\ + \\ M/80\text{-}K_2Cr_2O_7 \end{Bmatrix}$	0·350	6·62	$M/10$-H_3PO_4	0·062	1·80
			$M/10$-H_3AsO_4.........	0·065	1·85
			$M/10$-HCl	0·030	
$M/40$-$\begin{Bmatrix} KH_2BO_3 \\ H_3BO_3 \end{Bmatrix}$ ...	0·496	9·04*	$M/10$-$HMnO_4$.........	0·030	
$M/40$-$\begin{Bmatrix} KH_2AsO_3 \\ H_3AsO_3 \end{Bmatrix}$ ...	0·498	9·07			

* Denotes determined by hydrogen electrode.

The measurements of p_H in the buffer mixtures of phosphates, arsenates, and chromates, all half-neutralised with respect to the second hydrogen ion, give an interesting comparison of the strength of these acids. Various values for the second dissociation constant of phosphoric acid * have been calculated depending on the activities of the phosphates which are assumed (Hodgman and Lange, "Handbook of Chemistry and Physics," 9th edn., p. 422, give 2×10^{-7}; Cohn, *J. Amer. Chem. Soc.*, 1927, **49**, 192, gives $6{\cdot}9 \times 10^{-8}$). It seems probable, however, that the salts of all three of these acids would have about the same activity coefficients. If this is the case, the ratios of the hydrogen-ion concentrations of the half-neutralised buffer mixtures would be nearly equal to the ratio of the dissociation constants of the acids. On this assumption the above data indicate that

$$\frac{[H^\cdot][HPO''_4]}{[H_2PO_4']} : \frac{[H^\cdot][HAsO''_4]}{[H_2AsO_4']} : \frac{[H^\cdot][CrO_4'']}{[HCrO_4']} = 1 : 1{\cdot}2 : 1{\cdot}5;$$

$$\frac{[H^\cdot][AsO_2']}{[HAsO_2]} : \frac{[H^\cdot][BO_2']}{[HBO_2]} = 1 : 1{\cdot}1;$$

and

$$\frac{[H^\cdot][C_2H_3O_2']}{[HC_2H_3O_2]} : \frac{[H^\cdot][N_3']}{[HN_3]} = 1 : 1{\cdot}38.$$

If the constant for the second-stage dissociation of phosphoric acid is taken as $6{\cdot}9 \times 10^{-8}$, this would give $1{\cdot}03 \times 10^{-7}$ as the constant for the second dissociation constant of chromic acid, a value slightly lower than that obtained by Britton ($4{\cdot}4 \times 10^{-7}$) using the hydrogen and oxygen electrodes (J., 1924, **125**, 1572). It seems possible that the hydrogen electrode may have been giving slightly low p_H readings in Britton's measurements.

West (J., 1900, **77**, 705) calculated the dissociation constant of

azoimide from conductivity measurements and stated that it is an acid of "about the same strength as acetic"; the glass-cell results show that it is appreciably stronger.

The only value of the dissociation constant of hydrazine found in the literature was that of Bredig (*Z. physikal. Chem.*, 1894, **13**, 308); this was calculated from conductivity measurements and varied from $4 \cdot 4 \times 10^{-6}$ to $2 \cdot 1 \times 10^{-6}$ according to the dilution. The p_H of a solution containing $M/10\text{-}N_2H_5{\cdot}OH + M/10\text{-}N_2H_5Cl$ was found by comparison with phosphate and borate buffers at 23°:

	p_H.	Glass cell *E.M.F.*
Phosphate buffer	6·81	0·389
$M/10\text{-}N_2H_5Cl + M/10\text{-}N_2H_5{\cdot}OH$	8·24	0·469
Borate buffer	9·24	0·525

The dissociation constant corresponding to this p_H would be about $1 \cdot 7 \times 10^{-6}$ if complete dissociation of hydrazine hydrochloride is assumed; or $1 \cdot 4 \times 10^{-6}$ if 80% dissociation (analogous to that of other univalent salts) is assumed.

Hydrochloric and permanganic acids do not differ measurably in strength; this result is in agreement with the comparative strengths of these acids as measured by conductivity.

The dissociation constants thus calculated from hydrogen-ion activities of half-neutralised solutions are summarised below.

Assumed second-stage constant for H_3PO_4	$6 \cdot 9 \times 10^{-8}$ *
Second-stage constant for H_3AsO_4	$8 \cdot 3 \times 10^{-8}$
,, ,, ,, H_2CrO_4	$1 \cdot 0 \times 10^{-7}$
Assumed first-stage constant for H_3BO_3	$6 \cdot 5 \times 10^{-10}$ †
Calculated ,, ,, ,, H_3AsO_3	$6 \cdot 0 \times 10^{-10}$
Assumed constant for $HC_2H_3O_2$	$1 \cdot 86 \times 10^{-5}$ ‡
Calculated ,, ,, HN_3	$2 \cdot 56 \times 10^{-5}$
Dissociation constant for N_2H_5OH	$1 \cdot 4\text{—}1 \cdot 7 \times 10^{-6}$

* Cohn, *loc. cit.* † Landolt–Börnstein, 5te Aufl., p. 1132.
‡ Landolt–Börnstein, 5te Aufl., p. 1141.

Hydrolysis of Copper Sulphate.—O'Sullivan (*Trans. Faraday Soc.*, 1925, **21**, 319) measured the hydrogen-ion activity of copper sulphate solutions by means of the quinhydrone electrode. His *E.M.F.* readings changed with time in a direction indicating increasing acidity, and he attributed this to slow oxidation of the quinhydrone. It was found that the hydrogen-ion activity of such solutions as measured by the glass cell changed in a similar manner, indicating that the hydrolysis is probably a slow reaction. The more dilute solutions showed a similar increase after being boiled and cooled. The p_H of $M/20$-copper sulphate measured by the glass cell is 4·24, in fair agreement with O'Sullivan's value, 4·14.

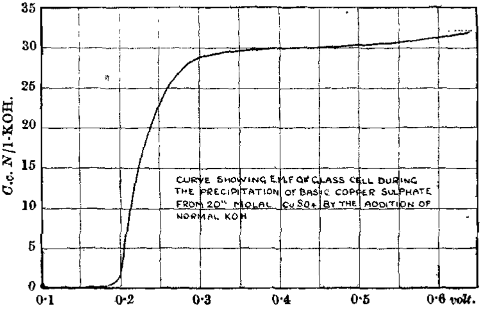
Measurements of various solutions are given in Table V.

TABLE V.

The hydrolysis of $CuSO_4$ solutions.

Solution.	E_g.	Diff.	p_H.	Temp.
Freshly made M-$CuSO_4$	0·110	0·067	3·43	25°
M/10-KAc + M/10-HAc	0·177		4·63	,,
M-$CuSO_4$, next day	0·144	0·068	3·42	,,
M/10-KAc + M/10-HAc, next day	0·212		4·63	,,
M-$CuSO_4$, 2 days later	0·138	0·074	3·31	,,
M/10-KAc + M/10-HAc, 2 days later ...	0·212		4·63	,,
25 C.c. M-$CuSO_4$ + 0·25 c.c. N-KOH, boiled and cooled	0·183	0·053	3·71	,,
M/10-KAc + M/10-HAc	0·236		4·63	,,
M/10-$CuSO_4$, fresh	0·215	0·021	4·27	,,
M/10-KAc + M/10-HAc	0·236		4·63	,,
M/10-$CuSO_4$, boiled	0·204	0·032	4·08	,,
M/10-KAc + M/10-HAc	0·236		—	,,
M/20-$CuSO_4$, fresh	0·231	0·006	4·53	18
M/10-KAc + M/10-HAc	0·237		4·63	
M/20-$CuSO_4$, boiled	0·213	0·023	4·24	,,
M/10-KAc + M/10-HAc	0·236		4·63	
M/20-$CuSO_4$, 2 days later	0·210	0·023	4·24	,,
M/10-KAc + M/10-HAc, 2 days later ...	0·233		—	

FIG. 5.



Glass cell E.M.F.

Britton (J., 1925, **127**, 2796) measured the *E.M.F.* of a copper electrode dipping into a copper sulphate solution during the precipitation of the basic sulphate by the addition of alkali. He found that a sudden change occurred when three-quarters of the alkali necessary to combine with all the sulphate radical had been added, and concluded that the precipitated basic sulphate had the composition $4CuO,SO_3,xH_2O$. Later Fowles (J., 1926, 1845) claimed *to have prepared other basic sulphates of copper.*

As the hydrogen-ion activity of a copper sulphate solution must be a function of the copper-ion concentration, there should be a sudden decrease in hydrogen-ion activity as well as copper-ion activity when almost all the copper has been precipitated as basic sulphate. The *E.M.F.* of a glass cell was therefore measured during the precipitation of basic copper sulphate by alkali, and the sudden rise in *E.M.F.* occurred at the stage noted by Britton (see Fig. 5 and Table VI). The initial rapid rise in *E.M.F.* on addition of a small quantity of alkali may be partly due to traces of free sulphuric acid; the remaining rise up to E_g 0·2 may be accounted for on the hypothesis that the reaction $3Cu^{\cdot\cdot} + 3H_2O + CuSO_4 = CuSO_4,3CuO + 6H^{\cdot}$ is very slow when the hydrogen-ion concentration is greater than 10^{-4}, and then suddenly accelerates, further small additions of alkali being almost without effect on the p_H of the solution until nearly all the copper has been precipitated (see Table VI).

TABLE VI.

Precipitation of basic copper sulphate at 25°.

Control solution: 20 C.c. of N-$CH_3{\cdot}CO_2H$ + 1 c.c. of N-KOH + 179 c.c. of water; E_g, 0·165; p_H by hydrogen electrode, 3·44. (This buffer mixture was emptied out and replaced by 20 c.c. of M-$CuSO_4$ solution.)

N-KOH added, c.c.	E_g.	N-KOH added, c.c.	E_g.	N-KOH added, c.c.	E_g.
0·05	0·164 *	10·0	0·212	28·6	0·292
0·15	0·178	15·0	0·222	29·5	0·361
0·5	0·190	20·0	0·237	30·0	0·464
2·0	0·200 †	25·0	0·261	30·5	0·502
5·0	0·206	27·5	0·281	32·0	0·636 ‡

* p_H = 3·33. † p_H = app. 4·06. ‡ Changing after 20 mins. to 0·613.

It was thought to be of interest to determine by means of the glass cell what changes in hydrogen-ion concentration take place in the iodide–iodate method for estimating small quantities of strong acids. It was found that, although the p_H continues to change for 20 mins. after the addition of the acid, this delayed change is so small that the analytical results are not appreciably different from those obtained by immediate titration of the iodine. Moreover, it is seen (Table VII) that the mixture attains neutrality after the addition of two-thirds of the amount of acid necessary to decompose all the iodate.

TABLE VII.

p_H of iodide–iodate mixture.

Solution.	E_g.	p_H, interpolated.
50 C.c. of (0·1M-KIO_3 + 0·8M-KI)	0·456	8·4
50 C.c. of (0·1M-KIO_3 + 0·8M-KI) + 20 c.c. of N-HCl	0·378	6·9
Phosphate buffer, p_H 6·81	0·363	—
Borate buffer, p_H 9·19	0·503	—

Summary.

1. Glass for use in Haber's cell should be as nearly as possible free from potash, alumina, and borates. A glass containing 72% SiO_2, 8% CaO, and 20% Na_2O proved very satisfactory. The bulb should be blown as rapidly as possible to avoid devitrification.

2. In acid solutions this glass gave no evidence of the "mixed electrode function" of Horovitz and Schiller. Its behaviour is best explained by the hypothesis that the hydrogen-ion concentration is maintained relatively constant within the glass phase by the buffer action of the sodium acid silicate in the glass. This buffer action begins to become less effective at about p_H 9, which is about the p_H of a sodium acid silicate buffer mixture half neutralised with respect to the first hydrogen ion of silicic acid (dissociation constant, 10^{-9}).

3. When the solution in contact with the glass is more alkaline than p_H 13, the glass surface is rapidly attacked. In this p_H range the second hydrogen ion of silicic acid (dissociation constant, 10^{-13}) begins to be neutralised, and as the glass surface is attacked the hydrogen-ion concentration within the glass falls rapidly, with a corresponding drop in the *E.M.F.* of the glass cell. Sodium hydroxide shows this effect more than potassium hydroxide; this might be partly due to a sodium-electrode function in the glass, but as lithium hydroxide has a similar effect, it is more reasonable to suppose that glass is more readily penetrated by sodium and lithium hydroxides than by potassium hydroxide, possibly because of smaller dimensions of the ions.

4. The following dissociation constants have been determined by measuring the p_H of half-neutralised buffer mixtures: the second-stage constants of arsenic and chromic acids ($8{\cdot}3 \times 10^{-8}$ and $1{\cdot}0 \times 10^{-7}$, respectively), the first-stage constant of arsenious acid (6×10^{-10}), and the constants of azoimide and hydrazine hydrate ($2{\cdot}56 \times 10^{-5}$ and $1{\cdot}4 \times 10^{-6}$, respectively).

5. The hydrogen-ion activity of copper sulphate solutions has been measured, and it has been shown that the hydrolysis of copper sulphate is a slow reaction at the ordinary temperature. It has also been shown that the basic sulphate of copper precipitated by alkali must have the composition $3CuO,CuSO_4,xH_2O$, in agreement with the results of Britton.

6. The p_H of an iodide–iodate mixture has been found to be about 6·9 after two-thirds of the iodate have been decomposed by the addition of hydrochloric acid.

Acknowledgments are due to Dr. E. K. Rideal for his many helpful suggestions, especially those concerning the buffer action of

glass and the possibility of the similarity between the action of lithium and sodium hydroxides. I also wish to thank Professor W. E. S. Turner, of Sheffield University, for his kindness in furnishing analysed samples of glass and for his suggestions as to the possible effects of aluminium oxide.

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LXV.—*Cyclic Organo-metallic Compounds. Part IV. Tellurylium Compounds* (continued).

By HARRY DUGALD KEITH DREW.

WHEN hydrated diphenoxtellurylium dibisulphate (I), or the complex (IV) which it forms with two molecules of sulphuric acid, is crystallised from glacial acetic acid, it is transformed to a deeply coloured, bronzed substance which was described (J., 1926, 3055) as *diphenoxtellurylium hydroxybisulphate monohydrate (II)*:

$$\text{(I.)}\quad \left[\left(C_6H_4<\substack{O\\Te}>C_6H_4\right)_2\right](HSO_4)_2,3H_2O \xrightarrow[\text{acid}]{\text{acetic}}$$

$$\left[\left(C_6H_4<\substack{O\\Te}>C_6H_4\right)_2\right](HSO_4)(OH),H_2O\quad \text{(II.)}$$

This substance (II) is decomposed by water into the constituent donor and acceptor, a reaction which was stated to be only approximately quantitative (*loc. cit.*), since the author obtained 46% of phenoxtellurine as acceptor instead of 40·9% demanded by theory. The method of analysis has now been improved, and, as a result, it is found that the decomposition by water is quantitative and that the true percentage of phenoxtellurine present as acceptor in the above compound is 53·5. The percentage of phenoxtellurine present in the donor form (not previously estimated) has been determined as 27·9. Two molecular proportions of phenoxtellurine are therefore present in the acceptor condition to one in the donor, and the substance formerly represented as (II) must now be described as *triphenoxtellurylium dibisulphate*, having the empirical formula (III).

The ultimate analytical figures calculated from the revised formula approximate closely to those required by the old formula and are in equally good agreement with the figures previously obtained by actual experiment:

%.	Old formula.	New formula.	Found (*loc. cit.*).
C	39·8	40·0	39·7, 39·6, 39·6
H	2·8	2·4	2·6, 2·5, 2·9
O	17·7	16·3	17·5
S	4·4	5·9	4·0, 4·9
Te	35·25	35·4	35·1

Whereas, however, the old formulation requires equal amounts (40·9%) of phenoxtellurine in donor and acceptor, the new formula requires 54·7% in the acceptor and 27·3% in the donor, figures which agree with those found by experiment.

The method has been applied also to the parent compounds of the series, with the result that the structures previously assigned to them have been confirmed:

	% Phenoxtellurine			
	in acceptor.		in donor.	
Compound.	*Calc.*	*Found.*	*Calc.*	*Found.*
Diphenoxtellurylium dibisulphate disulphuric acid trihydrate (IV)	28·5	28·7	28·5	27·8
Diphenoxtellurylium dibisulphate trihydrate (I)	35·2	34·9	35·2	35·6

The changes undergone by these substances can therefore be expressed empirically in the following simple manner:

$$\left[\left(C_6H_4{<}{}^{O}_{Te}{>}C_6H_4\right)_2\right](HSO_4)_2,2H_2SO_4,3H_2O \xrightarrow[\text{air}]{\text{moist}} (I.) \xrightarrow[\text{acid}]{\text{acetic}} \left[\left(C_6H_4{<}{}^{O}_{Te}{>}C_6H_4\right)_3\right](HSO_4)_2$$

(IV.) (III.)

Whereas the transformation of (IV) to (I) involves, as previously given, merely the removal of two molecules of sulphuric acid, that of (I) to (III) involves the elimination, from two molecules of (I), of three molecules of water and one molecule of trihydrated phenoxtellurine dibisulphate. This reaction can only occur after dissociation of (I) into its constituent donor and acceptor, a change which has already been shown to take place in glacial acetic acid solution (*loc. cit.*, p. 3061). Recrystallisation of (IV) or of (I) from hot acetic acid was already known to lead to the separation of a residue of basic phenoxtellurine sulphate, a phenomenon previously attributed to partial hydrolysis by moisture.

The new view of the transformation in acetic acid solution does not affect the theoretical considerations dealt with in the previous paper. The colour change undergone by the solution of compound (III) in acetic acid can be expressed by the equilibrium:

$$(III.) \underset{\text{conc. or cold}}{\overset{\text{dilute or hot}}{\rightleftharpoons}} 2C_6H_4{<}{}^{O}_{Te}{>}C_6H_4 + \left[C_6H_4{<}{}^{O}_{Te}{>}C_6H_4\right](HSO_4)_2$$

(soln. deep cherry-red) (soln. pale yellow)

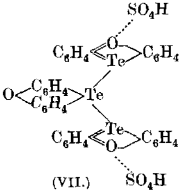
Since phenoxtellurine dibisulphate trihydrate may be represented by the simple formula (V), there exists a series of compounds of the

$$\left[\left(C_6H_4<^{O}_{Te}>C_6H_4\right)\right](HSO_4)_2,3H_2O \qquad \left[\left(C_6H_4<^{O}_{Te}>C_6H_4\right)_x\right](HSO_4)_2$$

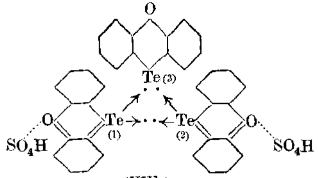
(V.) (VI.)

type (VI) in which x may be 1, 2, or 3, the various members of the series being associated with different addenda (H_2SO_4 or H_2O), or, as in (III), having no addendum. The molecule of each of these substances contains two anions, which make their appearance in a single molecule of the donor when the compound is decomposed by water, the remaining phenoxtellurine appearing as the acceptor. The ratio of phenoxtellurine in the acceptor to that in the donor is therefore $(x - 1) : 1$.

Expanded formulæ have already been given (*loc. cit.*) for compounds (I), (IV), and (V); it remains to consider compound (III). In this substance the third molecule of phenoxtellurine might be regarded as an addendum substituting $3H_2O$ in the formula of (I). It is considered probable, however, that the three tellurium atoms are actually linked together, either in a chain (VII) or in a ring (VIII). Of these alternatives, the second is preferred, since in it the three phenoxtellurine residues are equivalently situated if the formula be regarded as potentially dynamic. In the phase represented, the *tellurium atoms marked (1) and (2) supply each an electron to* affix tellurium atom (3), whilst they are themselves united by means



(VII.)



(VIII.)

of a non-polar bond (the dots show the binding electrons, and the arrows indicate the atoms whence these electrons originate; the *dotted bonds represent polar linkings). At all phases of the formula, each of the three tellurium atoms is seen to be associated with 56,* and each oxygen and carbon atom is associated with 10, electrons.

This view is seen to involve the suggestion that three atoms may be held together by the sharing of 4 electrons.

Thomason and the author (J., 1927, 119) described a compound which, from ultimate analysis, they considered a complex of

phenoxtellurine and 2-chloro-8-methylphenoxtellurine in molecularly equivalent proportion. This substance has now been separated into its constituents by the fractional precipitation of its chloroform solution with bromine. The phenoxtellurine is precipitated first, as the dibromide. Hence the introduction of the above nuclear substituents depresses the affinity of the tellurium atom for bromine.

The di-α-bromocamphor-π-sulphonate of chloromethylphenoxtellurine was prepared, but could not be purified owing to its tendency to hydrolyse. It yields brilliantly coloured tellurylium compounds with phenoxtellurine or substituted phenoxtellurines, so that it is necessary to add the α-bromocamphor-π-sulphonic acid anion to the list of mobile anions already given (J., 1926, 3064). From this list, for reasons which will now be apparent, the OH anion should be deleted.

EXPERIMENTAL.

Estimation of the Percentage of Phenoxtellurine present as Donor and as Acceptor in Tellurylium Compounds.—(1) *Triphenoxtellurylium dibisulphate* (III). The sample (0·5277 g.) was shaken in a stoppered extraction funnel with cold water (15 c.c.) and several times with chloroform. The filtered chloroform was allowed to evaporate at the ordinary temperature (loss of phenoxtellurine occurs at more elevated temperatures). The white aqueous suspension, treated with an excess of potassium metabisulphite, gave phenoxtellurine, which was extracted with chloroform (Found: phenoxtellurine as acceptor, 53·5; as donor, 27·9. Calc. for $C_{36}H_{26}O_{11}S_2Te_3$: phenoxtellurine as acceptor, 54·7; as donor, 27·3%).

(2) *Diphenoxtellurylium dibisulphate disulphuric acid trihydrate* (IV). The sample (0·5369 g.) was reduced with aqueous potassium metabisulphite, and the total phenoxtellurine extracted with chloroform: found, 0·3038 g. A second sample (1·7844 g.) was treated with cold water (50 c.c.) and nearly neutralised with *N*-sodium carbonate (12·9 c.c.). The acceptor phenoxtellurine was then estimated as before (Found: phenoxtellurine as acceptor, 28·75; as donor, 27·85. Calc. for $C_{24}H_{28}O_{21}S_4Te_2$: phenoxtellurine as acceptor, 28·55; as donor, 28·55%).

(3) *Diphenoxtellurylium dibisulphate trihydrate* (I). In a first sample (0·3380 g.), the total phenoxtellurine was estimated as above: found, 0·2383 g. A second sample (0·5261 g.) was treated with cold water (50 c.c.) and *N*/10-sodium carbonate (19 c.c.) as in (2) (Found: phenoxtellurine as acceptor, 34·9; as donor, 35·6. Calc. for $C_{24}H_{24}O_{13}S_2Te_2$: phenoxtellurine as acceptor, 35·2; as dor 35·2%). In every case, the recovered phenoxtellurine was to be pure.

Molecular Compound of Phenoxtellurine and Chloromethylphenoxtellurine: Separation into its Constituents.—The compound (8·4 g.) m. p. 59° (J. 1927, 119), was dissolved in chloroform (12 c.c.), and a solution of 2·1 g. of bromine in 20 c.c. of chloroform gradually added. Phenoxtellurine dibromide (6·4 g.) separated, and this gave on reduction phenoxtellurine which was pure after one crystallisation. The chloroform mother-liquor was precipitated again by 0·4 g. of bromine in 5 c.c. of chloroform, giving a mixture of the two dibromides. The chloroform mother-liquor from this was precipitated by 1·7 g. of bromine, yielding *chloromethylphenoxtellurine dibromide*, a yellow, crystalline substance which is very *sparingly soluble in chloroform; m. p. 315° (decomp.). Its reduction* by aqueous potassium metabisulphite takes place only very slowly compared with that of phenoxtellurine dibromide. The product (3·2 g.), consisting of *chloromethylphenoxtellurine*, crystallises from alcohol in minute, pale yellow, prismatic needles, m. p. 46—47° (Found: C, 45·2; H, 2·5. $C_{13}H_9OClTe$ requires C, 45·3; H, 2·6%). It is very soluble in organic solvents but insoluble in water. It forms a *dichloride*, pale yellow prisms, m. p. 300° (decomp.), from xylene; a *diacetate*, colourless needles, m. p. 230—232° (with frothing), from acetic acid; and a *dibisulphate*, cream-coloured scales, which acts as a donor towards tellurides, giving deep purplish-black tellurylium compounds.

Chloromethylphenoxtellurine dissolved in cold concentrated sulphuric acid to a deep maroon-red solution which evolved sulphur dioxide. On treating the solution with a little water and crystallising the resulting minute, dark red crystals from acetic acid, a dark blue-black, crystalline powder having a greenish-bronze lustre was obtained. A solution of this *tellurylium compound* in acetic acid had an intense reddish-purple colour, which became pale yellow on dilution or heating (reversible change).

The foregoing procedure for the separation of the complex compound into its constituents enables the yield of phenoxtellurine (obtained by the method described in J., 1926, pp. 230—231) to be increased, since the reduced by-products from that process can be further worked up for phenoxtellurine by treatment with bromine in chloroform solution.

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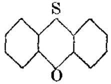
LXVI.—*Cyclic Organo-metallic Compounds. Part V. Phenoxselenine and Phenoxthionine from Phenoxtellurine. Selenylium and Thionylium Compounds.*

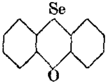
By HARRY DUGALD KEITH DREW.

PHENOXTHIONINE (I) was discovered by Mauthner (*Ber.*, 1906, **39**, 1344), who prepared it by a lengthy process from sodium thiopyrocatechol and 3-chloro-2 : 4-dinitrobenzoic acid. Phenoxselenine (II) has not hitherto been described.

The author's process for the preparation of phenoxtellurine (Part I; J., 1926, 223), *viz.*, condensation between diphenyl ether and the tetrachloride of the metalloid, followed by reduction with alkali bisulphite, cannot be applied in the case of phenoxthionine, and was fruitless in that of phenoxselenine, owing to the chlorinating action of selenium tetrachloride. It is now found, however, that phenoxtellurine may readily be transformed either to phenoxthionine or to phenoxselenine.

When phenoxtellurine is heated with an atomic proportion of sulphur, the red solution becomes greenish-brown (probably owing to the formation of the sulphide $C_6H_4{<}^{O}_{TeS}{>}C_6H_4$). An exothermic reaction then ensues; crystalline tellurium is set free, and is replaced by sulphur. The resulting phenoxthionine contains about 7% of unchanged phenoxtellurine, from which it is easily separated.

(I.) 

 (II.)

When selenium is employed instead of sulphur, the product consists of phenoxselenine (2 mols.) and phenoxtellurine (1 mol.). This mixture (or molecular complex) cannot be resolved by crystallisation, but pure *phenoxselenine* may be obtained from it quantitatively by transformation to the mixed dibromides, followed by warming with acetone.

Phenoxtellurine is totally recoverable from its dibromide, and therefore the foregoing reactions afford quantitative yields in the sense that the whole of the initial phenoxtellurine can ultimately be converted either into phenoxthionine or into phenoxselenine. The bulk of the tellurium can be recovered and used again.

The processes are probably applicable generally to the nuclear-substituted derivatives of phenoxtellurine. For example, 2-chloro-8-methylphenoxtellurine behaves towards sulphur in a manner similar to that of phenoxtellurine. The nitrophenoxtellurines,

which decompose explosively when heated with sulphur, afford an exception to this rule.

The following table shows a comparison between some of the properties of the foregoing substances:

Substance.	Colour.	M. p.	Colour in sulphuric acid.
Phenoxthionine	Colourless	58°	Intense violet
Phenoxselenine	Colourless	88	Intense olive-green; violet on dilution or warming (*reversible*)
Phenoxtellurine	Yellow (*from alcohol*); *orange* (*from acetic acid or acetone*)	79	Deep purplish-red

The three compounds, taken in pairs, form mixed crystals inseparable by solvents. Normal depression of melting point is therefore not shown by the mixtures. In fact, an admixture of all three compounds in about equal proportions melts between 55° and 85°. A similar relationship had been noticed previously (J., 1921, **119**, 1063) in the case of the crystalline acetylacetonates of aluminium, gallium, and indium—where the metallic atoms are related in the periodic table of the elements in the same manner as sulphur, selenium, and tellurium.

Phenoxthionine yields an *oxide*, $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{SO}{>}C_6H_4$ (III), (m. p. 158—159°), which gives with sulphuric acid a violet coloration, becoming deep blue on warming (irreversible). Further oxidation affords the dioxide, $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{SO_2}{>}C_6H_4$ (IV) (m. p. 147—148°), which gives no sulphuric acid coloration. This substance has already been prepared by Mauthner, who, however, gives m. p. 140—141° and states that a blue coloration is produced with sulphuric acid. His product was evidently contaminated with the oxide (III).

Phenoxthionine does not form a dichloride, dibromide, or diacetate.

Phenoxselenine forms an *oxide*, $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{SeO}{>}C_6H_4$ (V), which is soluble both in organic solvents and in water, separating from the latter as the crystalline neutral *dihydroxide*, $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{Se(OH)_2}{>}C_6H_4$ (VI). These substances give deep violet solutions in sulphuric acid, which become permanently blue on being warmed.

Phenoxselenine forms a yellow *dichloride*, and a red *dibromide*, $C_6H_4{<}\genfrac{}{}{0pt}{}{O}{SeBr_2}{>}C_6H_4$ (VII), and these compounds differ from the corresponding halides of phenoxtellurine (which are colourless and yellow respectively) in that they are halogenating agents towards such substances as acetone. Phenoxselenine forms only an unstable ... readily hydrolysed to the oxide.

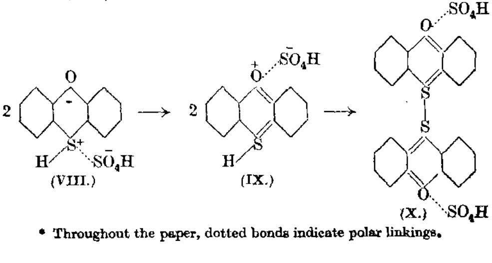
The oxides (III) and (V) differ remarkably in that, whereas phenoxthionine oxide is only sparingly soluble in water, may be distilled unchanged, does not catalytically decompose hydrogen peroxide, and is not reduced by alkali bisulphite, phenoxselenine oxide is extremely soluble in water, quantitatively loses oxygen on being heated above its melting point, liberates oxygen from hydrogen peroxide, and is at once reduced by alkali bisulphite in the cold.

Thionylium and Selenylium Compounds.

Hilditch and Smiles (J., 1911, **99**, 408) ascribed the intense colour of the sulphuric acid solutions of phenoxthionines and their oxides to the presence of thionium salts of the type $C_6H_4{<}{\substack{O(A)\\S(A)}}{>}C_6H_4$, where A stands for an acid radical. The following experiments show, however, that thionylium compounds (analogous to the tellurylium compounds) are in reality responsible.

When the intensely violet sulphuric acid solution of phenoxthionine is allowed to stand during three hours, until sulphur dioxide ceases to be produced, and is then decomposed with ice, half of the original phenoxthionine is recovered as the oxide (donor), the remaining half being recovered unchanged (acceptor). The coloured solution must therefore have been a homogeneous solution of a diphenoxthionylium compound, doubtless (by analogy with the corresponding tellurylium compound) in combination with sulphuric acid molecules.

It may be postulated that an additive compound * with sulphuric acid (VIII) is first produced and that this is transformed to the quinonoid form (IX) by the migration of its anion. Two molecules of (IX) are then oxidised by sulphuric acid to form a single molecule of *diphenoxthionylium dibisulphate* (X). The transformation of (IX) to (X) is thus similar in principle to the oxidation by sulphuric acid of thiophenol to diphenyl disulphide (Stenhouse, *Annalen*, 1869, **149**, 251).



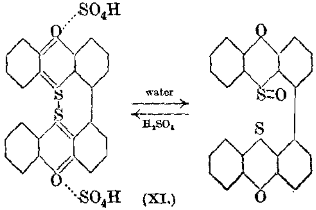
(VIII.) (IX.) (X.)

* Throughout the paper, dotted bonds indicate polar linkings.

On the above view, the change is seen to involve the transfer of an electron across the central ring of each phenoxthionine nucleus *from oxygen to sulphur*. The reaction may, however, be expressed in still simpler terms, if the suggestion (J., 1926, 3062) be adopted that reducing agents are substances which exchange electrons for anions. In that case, each molecule of the reducing agent, phenoxthionine, parts with an electron to sulphuric acid, receiving in exchange the bisulphate anion; the lost electron is then " replaced " by sharing (through the sulphur atoms) with another similar residue, giving (X). The nascent hydrogen, generated on receipt of the electron by a sulphuric acid molecule, is regarded as being directly removed by the excess of sulphuric acid.

It is a striking fact that a thionylium compound is produced when phenoxthionine oxide (III) is dissolved in sulphuric acid. The violet solutions of the oxide invariably yield phenoxthionine when decomposed by ice. Sulphuric acid acts, therefore, both as an oxidising agent towards the free sulphide and as a reducing agent towards its oxide, the reaction apparently ceasing when the thionylium state has been attained.

In the case of the oxide, however, secondary reactions ensue Fresh solutions of phenoxthionine oxide in cold sulphuric acid giv both phenoxthionine and its oxide after treatment with ice; bu from solutions allowed to stand during 2 hours oxide can no longe be recovered, the products then consisting of phenoxthionin equivalent to about one-third of the original oxide, together wit a yellow amorphous product. This substance, which is not sulphonic acid, gives an intensely blue colour with sulphuric aci and is therefore probably a nuclear-oxidation product of a thionyliu compound, *e.g.*, (XI).



(XI.)

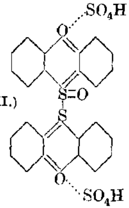
wh
Phe
$C_6H_4<$Se

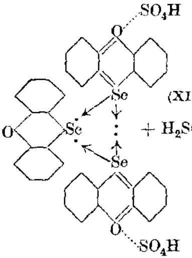
correspondi solution of phenoxthionine oxide in sulphuric aci
yellow respec the water-bath, *the violet colour changes to a perma*
such substanc the blue solution, diluted with water, yields phe
acetate, readil ivalent to only about one-quarter of the original o

the remaining product being similar to the above amorphous substance.

It is clear, therefore, that, although the action of sulphuric acid upon phenoxthionine oxide is complex, it invariably gives rise to thionylium compounds, which in part survive even when the solution is heated. Probably the first reaction consists in the formation of the oxythionylium compound (XII), a proportion of which loses persulphuric acid, giving the thionylium compound (X); while the remainder undergoes inner oxidation to (XI). The argument receives support from the fact that Fries and Volk (*Ber.*, 1909, **42**, 1170) have detected the formation of persulphuric acid when dimethylthianthrene oxide is dissolved in sulphuric acid.

(XII.)





(XIII.) $+ H_2SO_4 + 2H_2O$

Thionylium compounds are extremely sensitive to moisture, and are dissociated by acetic acid and by ether. Attempts to isolate them have proved fruitless.

Selenylium compounds, however, are less readily decomposed by water and it has been possible to isolate one of them in a pure crystalline condition.

The deep olive-green solution of phenoxselenine in cold sulphuric acid, decomposed by ice after 2 hours, gives only phenoxselenine (57·4% of the original weight) and phenoxselenine oxide (equivalent to 41·2% of phenoxselenine). The green solution may thus consist of triphenoxselenylium dibisulphate together with rather less than a molecular proportion of diphenoxselenylium dibisulphate, both probably in combination with sulphuric acid molecules.

Cautious dilution of such a solution with water gives two kinds of crystals, which are respectively deep copper-red (A) and dark purple (B). Conditions can be chosen in which only (A) is formed, but (B) has not been obtained free from (A). Recrystallisation from acetic acid does not alter the composition of (A), but crystal-

lisation of the mixture of (A) and (B) from acetic acid containing a drop of sulphuric acid transforms the whole into (A).

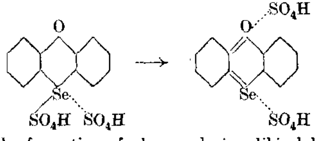
The red crystals consist of *triphenoxselenylium dibisulphate sulphuric acid dihydrate* (XIII; compare VIII in Part IV of this series; preceding paper). When decomposed by water, this substance gives only sulphuric acid, phenoxselenine (46·7%), and phenoxselenine oxide (equivalent to 23·0% phenoxselenine). Thus it contains two molecular proportions of phenoxselenine in the acceptor and one in the donor condition. Moreover, it yields 69·7% of total phenoxselenine, as against 69·35% demanded by theory.

The total sulphuric acid in this compound may be determined accurately by titration, whereas such is not the case with the tellurylium compounds, the sulphates of phenoxtellurine being less easily hydrolysed.

Compound (XIII) gives in acetic acid an intensely green solution which becomes almost colourless when warmed, and violet when heated to a higher temperature. Small amounts of added sulphuric acid increase the intensities of the colours. The feebly coloured solution may consist of the dissociated constituents (sulphuric acid, phenoxselenine, and phenoxselenine oxide); whereas the violet solution probably contains an oxyselenylium compound, analogous to (XII). The green solution contains the undissociated compound. This view is supported by the fact that the sulphuric acid solution of phenoxselenine oxide is violet, becoming permanently blue on being heated. The changes are analogous to those given by phenoxthionine oxide.

The purple crystals (B) consist either of a diphenoxselenylium compound or of the above substance (XIII) deprived of the molecule of attached sulphuric acid.

Phenoxselenine dibromide (VII) evolves hydrogen bromide when dissolved in concentrated sulphuric acid, giving a yellow solution which becomes orange-red on being warmed. On further warming, the solution becomes violet and then permanently blue. A similar behaviour is shown by the dichloride. The yellow colour is prob-

(XIV.)  (XV.)

ably due to the formation of phenoxselenine dihisulphate (XIV), which becomes orange-red when it assumes the quinonoid con-

dition (XV). Transformation to the oxyselenylium state (analogous to XII), with the accompanying changes already suggested, produces the violet colour, and inner oxidation to a complex (analogous to XI) represents the blue stage.

Phenoxtellurine dibisulphate gives blue or blue-black substances with warm phenoxthionine and with phenoxselenine in the cold, showing that mixed -ylium compounds, less stable than the telluryl-ium compounds, exist. The oxides of phenoxselenine and phenoxthionine act as acceptors towards phenoxtellurine dibisulphate when warmed, mixed oxy-ylium compounds probably being formed.

The study of thionylium, selenylium, and tellurylium compounds shows that, having regard to the three elements in their quadrivalent states, sulphur may be associated in its compounds with 18 or with 20 electrons, selenium with 36 or with 38 electrons, and tellurium with 54 or with 56 electrons. The tendency to become associated with the higher number of electrons decreases in the order Te, Se, S, as is shown by the diminishing stability of the corresponding -ylium compounds in the presence of water or organic solvents. It may be inferred that the tendency of oxygen to become associated with 12 electrons is even less than the tendency of sulphur to become associated with 20, but the possibility that -ylium compounds of oxygen are capable of existence in strongly acid solutions is by no means excluded.

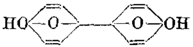
The stability of the oxides of phenoxthionine, phenoxselenine, and phenoxtellurine towards heat appears to decrease in the order S, Se, Te, but that of the dihalides, towards substances capable of halogenation and towards mineral acids, decreases in the order Te, Se, S. The stability towards heat of the dihydroxides appears to decrease in the order Te, Se, S; and the stability towards hydrolytic agents of such salts as the diacetates, dibisulphates, and dinitrates decreases in the same order.

The existence of -ylium salts makes it probable that "dimeric" structures of analogous nature are associated with the changes undergone by the thianthrens (Fries and Volk, *loc. cit.*), and by other substances containing similar ring systems.

Quinhydrones.

The compounds of the quinhydrone type simulate in many respects the behaviour of the tellurylium compounds, and it is accordingly suggested that the former substances possess a carbonylium structure. Quinhydrone itself, for example, may on this hypothesis be formulated as (XVI), its generator, quinol, being regarded as able to assume the carbonium phase (XVII). The latter molecule would be capable of passing to (XVI) either by

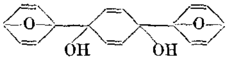
direct oxidation or by union with quinone. Replacement of the mobile hydrogen atom in (XVII) by an alkyl group would be expected to diminish the tendency towards quinhydrone formation, on account of the reluctance of the alkyl radical to assume a charge; and this accords with the experience that quinol dialkyl ethers form only unstable quinhydrones.

(XVI.) 

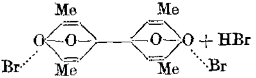
(XVII.)

The same considerations would apply to the compounds formed by diamines and alkylated diamines with quinones and quinone-imines, which would contain an imino-bridge. In the alkylated diamines, however, the alkyl groups would be more electropositive than those in the ethers. The *p*-quinonoid oxygen- or imino-bridge, unlike the simple *p*-bridge, is in conformity with stereochemical requirements for formulæ consisting of open chains of quinonoid benzene nuclei (*e.g.*, XVI), but not for closed chains of such nuclei. In cases of the latter type, perhaps, for example, in that of the compound of benzidine and quinonedi-imine, the bridge may be regarded as opened by the formation of a dipole. That the carbon–carbon linking in such a compound as (XVI) would be prone to ready disruption is rendered exceedingly probable by the recent work of Conant (*J. Amer. Chem. Soc.*, 1927, **49**, 2080). It has been shown, too, by Goldschmidt and Christmann (*Ber.*, 1924, **57**, 711) that a pair of salt-forming hydroxyl groups still exists in quinhydrone, for the deep blue sodium salt of this substance was isolated in the solid state. This is in agreement with the formulations now proposed.

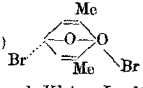
For phenoquinone the formula (XVIII) is suggested; and in the pyrone series, Hantzsch and Denstorff's perbromide of dimethylpyrone hydrobromide (*Annalen*, 1906, **349**, 39) may be regarded as possessing the structure (XIX), the donor in this case being the dimethylpyrone dibromide (XX) and the acceptor dimethylpyrone



(XVIII.)

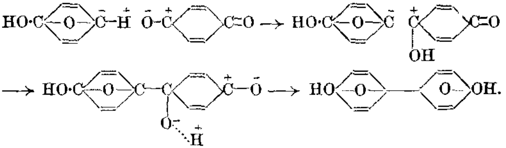


(XIX.)

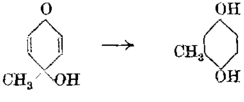
(XX.) 

itself (compare Collie and Klein, J., 1927, 2162). The donor therefore parts with an anion, as in the case of the phenoxtellurine

and similar salts; whereas, in the formation of true quinhydrones, the donor is probably to be regarded as parting with a kation. Since in some instances aromatic hydrocarbons, such as durene and hexamethylbenzene, form quinhydrones with suitable quinones, the substituted benzene nucleus must be capable of parting with charged hydrogen or alkyl. It may be noted that a mixture of a quinone with a quinol of another series contains the quinone of the latter series (Siegmund, *J. pr. Chem.*, 1915, **92**, 342), so that it is evident that hydrogen exchange occurs from quinol to quinone in accord with the scheme outlined above. In all of the cases cited, the negatively charged oxygen atom of the quinone or other ketone (or the nitrogen atom of the quinoneimine) is regarded as receiving the kation, the nuclei then joining owing to the attraction between the negative and the positive carbon atoms. The suggested process may be illustrated as follows for the formation of quinhydrone:



In toluquinol (XXI), the carbon–carbon linking is unstable, the compound isomerising in presence of alkali to (XXII) (compare Bamberger, *Annalen*, 1912, **390**, 164).

(XXI.)  (XXII.)

E X P E R I M E N T A L.

Phenoxthionine (I).—Phenoxtellurine (3 g.) and sulphur (0·35 to 0·4 g.) were heated together until reaction set in. This having ceased, the organic product was boiled during 10 minutes, and then distilled; or it was cooled and extracted by ether or chloroform. The product (2·1 g.) separated from acetic acid in pale yellow needles, m. p. 57—58°, unaltered by further crystallisation. The crystals contained 6—7% of unaltered phenoxtellurine (Found: C, 69·8, 70·0; H, 3·9, 4·0%). Purification was effected by dissolving the substance in chloroform, adding a few drops of bromine, filtering the solution, and allowing the solvent to evaporate; the residue was then warmed with a little acetone (which was allowed

o evaporate), taken up in ether, and filtered. From alcohol, it ormed inch-long, colourless, refractive, prismatic needles or plates, n. p. 58° after slight shrinkage from 56°. Mauthner (*loc. cit.*) gives m. p. 60—61°; but purification of the present author's product by several methods failed to raise the melting point (Found: C, 71·7, 71·8; H, 4·1, 4·0. Calc. for $C_{12}H_8OS$: C, 72·0; H, 4·0%).

Phenoxthionine oxide (III) is prepared by adding a slight excess of hydrogen peroxide to a glacial acetic acid solution of phenoxthionine, warming the mixture for a few minutes, and diluting it somewhat with water. The oxide forms colourless massive needles or prisms from acetic acid or benzene, is rather sparingly soluble in hot water to a neutral solution, and does not form a hydroxide. It forms phenoxthionine when treated with zinc dust and acetic acid; and is reduced also by warm acetic-hydrochloric acids, evolving chlorine, which partly chlorinates the resulting phenoxthionine. It melts at 158—159°, and gives a deep violet coloration in warm, syrupy phosphoric acid (Found: C, 66·8; H, 3·7. $C_{12}H_8O_2S$ requires C, 66·7; H, 3·7%).

Phenoxthionine dioxide (IV) is prepared by the prolonged action of hydrogen peroxide upon phenoxthionine in glacial acetic acid, or by the action of chromic acid or potassium permanganate. It forms long, colourless needles, m. p. 147—148°, from dilute acetic acid, and is unaltered even when dissolved in hot sulphuric acid. It is very resistant to reducing agents and appears quite unaffected by hot acetic-hydrochloric acids (Found: C, 61·9; H, 3·3; S, 13·4. $C_{12}H_8O_3S$ requires C, 62·05; H, 3·5; S, 13·8%).

Action of Sulphuric Acid upon Phenoxthionine.—Phenoxthionine (0·3752 g.) was dissolved in cold concentrated sulphuric acid (5 c.c.). The deep violet solution was kept for 3 hours, the evolved sulphur dioxide being drawn off under reduced pressure. The solution was then cooled in ice and salt, and decomposed by ice (30 g.). The colourless suspension was filtered, and the filtrate extracted with chloroform; the filter-paper was washed with chloroform. The total amount of solid recovered (dried over phosphorus pentoxide) was 0·3798 g. From it the phenoxthionine (0·1891 g., m. p. 57—58°) was extracted quantitatively by cold light petroleum (b. p. 40—60°). The residue of almost pure phenoxthionine oxide (m. p. 155—156°, after one crystallisation from dilute acetic acid) amounted to 0·1875 g. These results show that phenoxthionine and its oxide are present in molecular proportion in the coloured solution. Moreover, these two substances must be combined, since neither is stable towards sulphuric acid in the free condition. A *thionylium compound* (X) is therefore present.

Action of Sulphuric Acid on Phenoxthionine Oxide.—(1) Phenox-

thionine oxide (0·3902 g.) was dissolved in concentrated sulphuric acid (5 c.c.); sulphur dioxide was not evolved, nor was the evolution of oxygen detected. The intensely purplish-violet solution was kept during 2 hours and then decomposed with ice (20 g.). The recovered brown solid gave pure phenoxthionine (0·1247 g.) on extraction with cold petroleum. The brown insoluble residue (0·2658 g.), probably containing a little phenoxthionine oxide, could not be separated into pure constituents. The more sparingly soluble portion, left after extraction with cold acetone, was a brown, amorphous solid, m. p. 215—220° (decomp.), which gave an intensely blue coloration with cold sulphuric acid. This substance is considered to be a complex of the type represented in formula (XI). It is clear that the phenoxthionine recovered could not have been present as such in the sulphuric acid solution, otherwise sulphur dioxide would have been evolved. The experiment thus showed that a thionylium compound was produced.

(2) Phenoxthionine oxide (0·3215 g.) in concentrated sulphuric acid (4 c.c.) was heated on a water-bath during $\frac{1}{2}$ hour, until the violet colour became blue; some sulphur dioxide was liberated. Decomposition with water led to the isolation of pure phenoxthionine (0·0883 g.). The remaining product was similar to the amorphous substance in (1).

(3) When a solution of phenoxthionine oxide, similar to that in (1) above, was kept for only 5 minutes before decomposition with ice, both phenoxthionine and phenoxthionine oxide were isolated from it in the pure condition, but a proportion of the amorphous substance was nevertheless produced.

Phenoxselenine (II).—Phenoxtellurine (3 g.) and powdered black selenium (0·9—1·3 g.) were mixed and heated so that the phenoxtellurine boiled gently during $\frac{1}{2}$ to 1 hour. The organic product (2·6 g.) was distilled, or extracted with ether or chloroform. It crystallised from acetic acid in long, sulphur-yellow needles, m. p. 82—84°, and was a mixture or compound containing about 2 mols. of phenoxselenine to 1 mol. of phenoxtellurine (Found: C, 54·9, 55·1; H, 3·1, 3·2%). It was resolved into its constituents by dissolving it in cold chloroform and adding a slight excess of bromine, collecting the mixed dibromides, and boiling them with acetone for a few minutes under reflux. The acetone and bromoacetone were allowed to evaporate, and the residue was taken up in ether and filtered from the insoluble phenoxtellurine dibromide. The ethereal solution left almost pure phenoxselenine. *Phenoxselenine* separates from alcohol or acetic acid in long, colourless, refractive, rectangular prisms, m. p. 87—88°, which have a faint odour of rose leaves (Found: C, 58·2; H, 3·3; Se, 31·1. $C_{12}H_8OSe$ requires C, 58·3;

H, 3·25; Se, 32·0%). It forms halides when treated with the halogen elements, dissolved in chloroform.

Phenoxselenine dichloride crystallises in light yellow, glistening plates, m. p. 127° (decomp.), from acetic acid. *Phenoxselenine dibromide* (VII) forms orange-red spangles, m. p. 147—148° (decomp.), from acetic acid. These halides give no coloration when ground with phenoxtellurine, even on being warmed.

Phenoxselenine oxide (V) was prepared by dissolving phenoxselenine in warm glacial acetic acid and adding a slight excess of hydrogen peroxide. The solution of the unstable diacetate was allowed to evaporate in the air, the crude product dissolved in a little hot water, and the solution allowed to cool undisturbed and then rapidly extracted with its own bulk of ether (to remove traces of unchanged phenoxselenine). The aqueous layer now crystallised, on scratching, in inch-long, slender, colourless needles of *phenoxselenine dihydroxide* (VI), very readily soluble in water (Found for air-dried substance: C, 51·25; H, 3·8. $C_{12}H_{10}O_3Se$ requires C, 51·2; H, 3·6%). The dihydroxide loses a molecule of water when dried at 100° in a vacuum over phosphorus pentoxide (Found, using 60 mg. of substance: loss of H_2O, 7·4. Calc., 6·4%), forming *phenoxselenine oxide* (V), a colourless, crystalline powder, m. p. 171—172°. Water changes it again to the dihydroxide, the aqueous solution of which is neutral. Above its melting point, the oxide is quantitatively transformed to phenoxselenine. Both the oxide and the dihydroxide vigorously decomposed hydrogen peroxide in glacial acetic acid solution (Found for the vacuum-dried oxide: C, 54·4; H, 3·15. $C_{12}H_8O_2Se$ requires C, 54·7; H, 3·05%). The dihydroxide is devoid of special bactericidal activity.

Action of Sulphuric Acid on Phenoxselenine.—The deep olive-green solution of phenoxselenine (0·2490 g.) in concentrated sulphuric acid (4 c.c.) evolved sulphur dioxide. After 2 hours, it was cooled in ice-salt and completely decomposed by ice. The colourless precipitate was filtered off, dried, and extracted by chloroform, the chloroform solution being then warmed with water; the solvent was allowed to evaporate, and the dried residue extracted by cold light petroleum (b. p. 40—60°), to free it from a little insoluble phenoxselenine oxide, which was then added to the aqueous solution. The petroleum left almost pure phenoxselenine (0·1429 g.), m. p. 85—88°, representing the acceptor portion. The aqueous solution and washings were then reduced with potassium metabisulphite and the donor portion of phenoxselenine (m. p. 85—88°) was estimated as before: found, 0·1025 g. The donor portion cannot in this case be estimated as phenoxselenine oxide, owing to the great solubility of this compound in water.

Triphenoxselenylium Dibisulphate Sulphuric Acid Dihydrate (XIII). –*Preparation.* (1) The deep greenish-black solution of phenoxselenine (1 g.) in concentrated sulphuric acid (6 c.c.) was warmed ently during 5 minutes, sulphur dioxide escaping. To the cooled quid, water (4 c.c.) was gradually added with stirring. After 6 hours, the copper-red crystals were filtered off through sintered lass, and rapidly spread on dried porous plate in a desiccator. 'he mother-liquor gave a further crop of the crystals when treated ith more water (3 c.c.).

(2) Phenoxselenine (0·8 g.) in concentrated sulphuric acid (7 c.c.) as left during 3 hours and then treated with water (7 c.c.). After tanding, the liquid deposited a crop of the copper-red crystals. 'he mother-liquor, treated with more water (4 c.c.), now gave on tanding a mixture of the copper-red crystals with bronzed-purple rystals. On recrystallisation from hot glacial acetic acid conaining a few drops of sulphuric acid, this mixture gave only the opper-red crystals.

The triphenoxselenylium compound forms large, deep copper-ed, rectangular tablets from acetic acid, the crystals giving a urplish-black powder. In a sealed tube, the powder changes near 55°, and then melts at 168° to a deep greenish-black liquid. The olution in sulphuric acid is olive-green, becoming violet on dilution r warming (reversible change). The substance is stable in moist ir for only a few hours, being then gradually hydroxylated with oss of colour. Analysis showed that the substance was unaltered merely purified) by crystallisation from acetic acid (Found in unecrystallised substance: C, 38·8; H, 3·15. Found in substance rystallised from acetic acid alone: C, 40·5; H, 3·3; S, 8·6. Found n substance crystallised from acetic acid containing sulphuric cid: C, 40·4; H, 3·1; S, 8·65. $C_{36}H_{32}O_{17}S_3Se_3$ requires C, 40·4; I, 3·0; S, 9·0%).

Hydroxylation of the Triphenoxselenylium Compound.—On treatment with cold water the substance breaks up quantitatively into ulphuric acid, phenoxselenine, and phenoxselenine oxide.

(1) Specimen crystallised from acetic acid alone: 0·2576 g., reated with 10 c.c. of water and titrated in presence of methyl-range, required 13·8 c.c. of *N*/10-sodium carbonate. The acceptor henoxselenine (m. p. 87—88°) was extracted with ether: found, ·1200 g. Hence 1 g. requires 53·6 c.c. of *N*/10-alkali; and acceptor henoxselenine amounts to 46·6%.

(2) Specimen crystallised from acetic acid containing a few drops f sulphuric acid: 0·5237 g., treated with 20 c.c. of water, required 8·2 c.c. of *N*/10-caustic soda. The acceptor phenoxselenine (m. p. 7—88°) amounted to 0·2446 g. The aqueous liquid was reduced

with potassium metabisulphite, and the donor phenoxselenine (m. p. 87—88°) extracted with chloroform : found, 0·1205 g. Hence 1 g. requires 53·9 c.c. of $N/10$-alkali; acceptor phenoxselenine amounts to 46·7%; donor phenoxselenine to 23·0%; and total phenoxselenine to 69·7%.

From the formula $C_{36}H_{32}O_{17}S_3Se_3$ is calculated : 1 g. requires 56·1 c.c. of $N/10$-alkali; acceptor phenoxselenine, 46·2%; donor phenoxselenine, 23·1%; and total phenoxselenine, 69·35%.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, November 14th*, 1927.]

LXVII.—*Silver Nitrate Concentration Cells in Acetonitrile and Benzonitrile.*

By FREDERICK KARL VICTOR KOCH.

THE Nernst formula for concentration cells

$$E = 2(1 - n_k)RT/nF \cdot \log_e C_1/C_2 \quad . \quad . \quad . \quad . \quad (1)$$

(where n_k is the transport number of the kation for primary electrodes, and C_1 and C_2 are the concentrations of the ions in the two solutions) has received good confirmation for aqueous solutions. It was first tested for non-aqueous solutions by Kahlenberg (*J. Physical Chem.*, 1900, **4**, 709), who investigated concentration cells of silver nitrate and cadmium iodide in acetonitrile and pyridine. The discrepancies between the observed and the calculated *E.M.F.*'s were large, except for silver nitrate in acetonitrile, and Kahlenberg concluded that the Nernst formula was not applicable to non-aqueous solutions. It is known, however, that complex conditions exist both in solutions of cadmium iodide in acetonitrile (Koch, J., 1927, 647) and in solutions of silver nitrate in pyridine (Abegg and Neustadt, *Z. physikal. Chem.*, 1909, **69**, 486), although Sakhanov and Grünbaum (*J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1794) found that the Nernst formula was obeyed in the latter case if the solutions were sufficiently dilute. Wilson (*Amer. Chem. J.*, 1906, **35**, 78) found that although solutions of silver nitrate in ethyl alcohol conformed to the Nernst formula, its solutions in methyl alcohol showed deviations from the theory. Grant and Partington (*Trans. Faraday Soc.*, 1923, **19**, 414), however, have shown that the theory is accurately obeyed in the latter solvent. The Nernst formula has further been confirmed for silver nitrate concentration cells in acetone (Roshdestwensky and Lewis, J., 1912, **101**, 2094), ethyl alcohol (Pearce and Farr, *J. Physical Chem.*, 1914, **18**, 729; Krumreich, *Z. Elektrochem.*, 1916, **22**, 446), and ammonia (Cady, *J. Physical Chem.*, 1905, **9**, 477).

The following results for silver nitrate concentration cells in acetonitrile and benzonitrile at 0° and 25° likewise support the Nernst formula, and show that the solution laws are obeyed in these solvents at least as nearly as in water.

Experimental.

Materials.—Acetonitrile and benzonitrile were purified as previously described (J., 1927, 647; this vol., p. 269); they had specific conductivities of $0{\cdot}5$—$1{\cdot}0 \times 10^{-7}$ and $0{\cdot}5 \times 10^{-7}$ mho, respectively, at 25°. Atomic-weight silver nitrate was kindly supplied by Dr. H. F. Harwood. The most concentrated solution ($N/10$ approx.) was made up by weight and the others by volume-dilution.

Apparatus.—The conductivity apparatus was the same as that previously described (*loc. cit.*, 1927). The *E.M.F.*'s were measured by the usual Poggendorff compensation method. The bridge wire (10 m. long), which was of the drum type (Leeds and Northrup), was calibrated by the method of Strouhal and Barus. The standard Weston cell was checked against other standard cells during the course of the investigations. Since the *E.M.F.*'s were small, they were measured in series with the standard cell in order to throw the zero point on to the centre of the bridge. Owing to the high resistance of these non-aqueous solutions, it is necessary to employ a high-resistance null instrument. Mudford's electromagnetically shielded galvanometer, with a resistance of 10,000 ohms, proved quite satisfactory.

The special all-glass cell was similar to that described by Krumreich (*loc. cit.*), and could be entirely immersed in the thermostat. The electrodes were inserted by means of ground-in joints and the liquid–liquid junction bridge was made as short as possible in order to reduce the resistance of the cell to a minimum. The electrodes consisted of silver foil wound round glass tubing; they were coated with a compact layer of crystalline silver by plating in a concentrated aqueous solution of silver nitrate, an even deposit being obtained by surrounding the electrode with a cylinder of silver foil. A platinum wire, which was fused to the silver foil, was connected through the bottom of the glass tube to the mercury–copper contact within.

Limits of Accuracy.—The *E.M.F.*'s in benzonitrile could be reproduced to about 0·5 millivolt, but those in acetonitrile only to about 1·0 millivolt; they have, however, been reduced in both cases to the nearest millivolt. The results given are the most consistent of several series which were recorded. The specific conductivity of every solution used was determined at 0° and 25° and the errors which would otherwise be introduced by intra- or extra-

polation were thus avoided. The conductivity readings may be considered accurate to 0·1%, and since in the calculation of the *E.M.F.*'s only the specific conductivities themselves are used, all errors inherent in weighings, determination of density, etc., are automatically eliminated.

Results and Discussion.

In the following tables Q_1 and Q_2 are the weights of solvent (in kg. per g.-mol. of silver nitrate), and κ_1 and κ_2 are the specific conductivities (in mhos) of the two electrode solutions.

Acetonitrile.

Q_1.	Q_2.	$\kappa_1 \times 10^3$.	$\kappa_2 \times 10^3$.	E (obs.).	n_k.	E (calc.).
			At 25° ± 0·01°.			
487	8·21	0·2672	5·970	0·086	0·461	0·087
,,	16·4	,,	3·775	0·075	0·449	0·074
,,	32·8	,,	2·332	0·059	0·470	0·061
,,	65·7	,,	1·387	0·047	0·445	0·046
,,	121	,,	0·7958	0·030	0·465	0·031
,,	243	,,	0·4444	0·012	(0·540)	0·014
				Mean	0·458	
			At 0° ± 0·01°.			
487	8·21	0·2082	4·992	0·083	0·445	0·082
,,	16·4	,,	3·139	0·068	0·467	0·070
,,	32·8	,,	1·919	0·056	0·464	0·057
,,	65·7	,,	1·124	0·044	0·445	0·043
,,	121	,,	0·6339	0·029	0·446	0·029
,,	243	,,	0·3491	0·012	(0·506)	0·013
				Mean	0·453	

Benzonitrile.

Q_1.	Q_2.	$\kappa_1 \times 10^4$.	$\kappa_2 \times 10^4$.	E (obs.).	n_k.	E (calc.).
			At 25° ± 0·01°.			
640	10·0	0·3295	4·823	0·076	0·451	0·074
,,	20·0	,,	2·948	0·061	0·459	0·060
,,	40·0	,,	1·880	0·049	0·468	0·048
,,	80·0	,,	1·237	0·036	0·467	0·036
,,	160	,,	0·7716	0·023	0·474	0·024
,,	320	,,	0·5217	0·012	0·475	0·013
				Mean	0·466	
			At 0° ± 0·01°.			
640	10·0	0·2221	3·134	0·069	0·446	0·067
,,	20·0	,,	1·963	0·056	0·450	0·055
,,	40·0	,,	1·274	0·045	0·457	0·044
,,	80·0	,,	0·8459	0·034	0·462	0·034
,,	160	,,	0·5194	0·021	0·473	0·022
,,	320	,,	0·3521	0·011	0·475	0·012
				Mean	0·461	

The assumption has been made that the ionic concentration m be deduced from conductivity measurements. We then have

$$C_1/C_2 = \alpha_1 N_1/\alpha_2 N_2 \quad . \; . \; . \; . \; . \; . \; ($$

where α_1, α_2 are the degrees of ionisation and N_1, N_2 are the normalities of the two solutions, respectively.

$$\begin{aligned} &\text{But} \quad \alpha_1 = \Lambda_1/\Lambda_\infty\,,\ \alpha_2 = \Lambda_2/\Lambda_\infty \\ &\text{and} \quad \Lambda_1 N_1 = \kappa_1,\ \Lambda_2 N_2 = \kappa_2 \end{aligned} \quad . \quad . \quad . \quad . \quad (3)$$

where Λ_1 and Λ_2 are the molecular conductivities corresponding to the normalities N_1 and N_2, and Λ_∞ is the molecular conductivity at infinite dilution. By inserting (3) in (2) and (2) in (1)

$$E = 2(1 - n_k)RT/F \,.\, \log_e \kappa_1/\kappa_2 \quad . \quad . \quad . \quad . \quad (4)$$

for a silver nitrate concentration cell ($n = 1$).

We have thus eliminated Λ_∞ and require only the values of the specific conductivities of the two solutions and that of the transport number in order to calculate the *E.M.F.*'s. The transport number of the silver ion for silver nitrate solutions in acetonitrile has been found by Schlundt (*J. Physical Chem.*, 1903, **6**, 189), using the direct Hittorf method, to be 0·448 and 0·471 for $N/11$- and $N/35$-solutions, respectively; but H. H. Morgan (in this laboratory; unpublished) obtained the values 0·442 and 0·448 at the same concentrations, showing a considerably smaller variation with dilution. Since no values of the transport number of the silver ion in benzonitrile are recorded in the literature, a determination was made for an $N/10$-solution by the usual method and found to be 0·396 (mean of 0·392 and 0·400). Determinations in more dilute solutions are untrustworthy owing to the high electrical resistance. The figures for n_k in the sixth column of the tables were deduced by comparing the observed *E.M.F.* with the *E.M.F.* calculated on the basis of the formula $E = RT/F \,.\, \log_e \kappa_1/\kappa_2$. The mean value of n_k was then used to obtain E (calc.) by formula (4).

It will be observed that the values of n_k for acetonitrile lie near to those obtained by Schlundt and Morgan, and those for benzonitrile, although higher than the value obtained by the direct method for an $N/10$-solution, are nearly the same as n_k for acetonitrile. It has in fact been shown by Walden ["Elektrochemie Nichtwässeriger Lösungen, 1924, p. 185; see also Carrara, *Gazzetta*, 1903, **33**, (ii), 241], on the basis of the expression $u\eta = k$ (where u is the mobility of an ion, η the viscosity of the solvent, and k a constant), that the transport number of an ion in a given salt should be independent of the solvent.

In conclusion, the author wishes to express his best thanks to Professor J. C. Philip, F.R.S., for his interest and kindly criticism during the course of this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, January 20th, 1928.*]

NOTES.

Allyl Hexoate and Octoate. By VENANCIO DEULOFEU.

ALLYL iodide (30 g.) was gently boiled for 2 hours with silver hexoate (42 g.). The liquid product was separated from the silver compounds by means of ether and distilled. The fraction (24 g.), b. p. 186—188°, was regarded as *allyl hexoate* and was analysed after redistillation (yield, 75%) (Found: C, 69·3; H, 10·4. $C_9H_{16}O_2$ requires C, 69·2; H, 10·2%). *Allyl octoate*, b. p. 225—230°, was similarly prepared from silver octoate (yield, 71%) (Found: C, 71·3; H, 10·6. $C_{11}H_{20}O_2$ requires C, 71·7; H, 10·8%). Both esters are oily compounds with a slightly pungent odour.—RIVADAVIA 5758, BUENOS AIRES. [*Received, December 31st*, 1927.]

Composition of Bleaching Powder. By CHARLES T. KINGZETT.

O'CONNOR's statement (J., 1927, 2700) to the effect that I considered the constitution of the calcium hypochlorite I had prepared from bleaching powder (J., 1875, **28**, 404) as $Ca(ClO)_2,4H_2O$ requires correction. The formula in question represented only the composition of the substance as separated in a more or less wet condition and not its *constitution*. That it was a hydrate of calcium hypochlorite there could be little doubt, but I confined my claims to the facts (1) that this compound had not previously been prepared in a solid state, (2) that it had been prepared from bleaching powder in the manner described, and (3) that analysis of the compound, rapidly dried between sheets of filter-paper but mechanically associated with some water, had the composition represented by $Ca(ClO)_2$, $4H_2O$.—[*Received, December 8th*, 1927.]

The Rearrangement of Benzyl Phenyl Ether. By WALLACE FRANK SHORT.

WHEN benzyl phenyl ether is heated to 225° in presence of anhydrous zinc chloride, or to 180° if a stream of hydrogen chloride is also passed through the mixture, a vigorous reaction occurs. The product, on distillation under diminished pressure, yields phenol, *o*-hydroxydiphenylmethane (m. p. 54°; phenylurethane, m. p. 118°), *p*-hydroxydiphenylmethane (m. p. 84—84·5°; identified by conversion into *p*-methoxybenzophenone, m. p. 61—62°), and products of high boiling point. Since phenol is produced, it is probable that the reaction follows a course similar to the Hofmann rearrangement of alkylanilines, benzyl chloride being formed as an intermediate. The investigation will be extended to substituted benzyl phenyl ethers containing substituents in both benzene nuclei.—UNIVERSITY COLLEGE, AUCKLAND, NEW ZEALAND. [*Received, December 7th*, 1927.]

LXVIII.—*The Isomerism of the Oximes. Part XXXIII. The Oximes of Opianic Acid and of Phthalic Anhydride.*

By Oscar L. Brady, Leslie C. Baker, Richard F. Goldstein, and Samuel Harris.

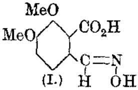
The oxime of opianic acid (I) was first obtained by W. H. Perkin, jun. (J., 1890, **57**, 1070) by the action of hydroxylamine on an alkaline solution of opianic acid. When, however, hydroxylamine hydrochloride acts upon opianic acid in aqueous alcohol at room temperature, opianic oxime anhydride (II) is produced (Liebermann, *Ber.*, 1886, **19**, 2278, 2923). Both the oxime and its anhydride on fusion are converted into hemipinimide with the evolution of much heat, and the same change occurs when they are heated with solvents containing a trace of acid (Liebermann, *loc. cit.*; Perkin, *loc. cit.*; compare also Liebermann and Stohmann, *Ber.*, 1892, **25**, 89; Roth, *Z. Elektrochem.*, 1910, **16**, 657).

It was thought that further investigation of this change might produce some evidence which would enable a decision to be made between Hantzsch's configurations for the aldoximes and those more recently suggested (Beckmann, Liesche, and Correns, *Ber.*, 1923, **56**, 341; von Auwers and Ottens, *Ber.*, 1924, **57**, 446; Brady and Bishop, J., 1925, **127**, 1357).

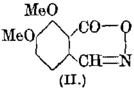
R·CH	R·CH	R·CH	R·CH
HO·N	N·OH	N·OH	HO·N
α-Oxime	β-Oxime	α-Oxime	β-Oxime
Hantzsch		New configurations	

Opianic oxime exists only in one form and behaves in a similar manner to α-aldoximes. The best method of distinguishing between α- and β-aldoximes cannot be applied, since on treatment with acetic anhydride opianic oxime gives, not an acetyl derivative, but opianic oxime anhydride, even when special precautions are taken. However, by the action of 2 : 4-dinitrochlorobenzene on the sodium salt of opianic oxime the dinitrophenyl ether is formed, as is the case with α-benzaldoxime and substituted α-benzaldoximes, whereas β-benzaldoxime gives the aldehyde on treatment with this reagent (Brady and Truszkowski, J., 1924, **125**, 1087). There is, moreover, no reason to suppose that in the formation of opianic oxime there is any exception to the, so far, invariable experience that the action of an alkaline solution of hydroxylamine on an aldehyde in which the aldehyde group is directly attached to the benzene ring produces the α-aldoxime.

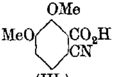
Adopting the new configurations, opianic oxime must, therefore, be represented as (I).



(I.)

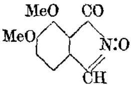


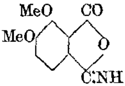
(II.)



(III.)

(IV.)

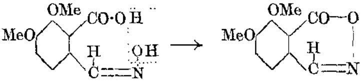




(V.)

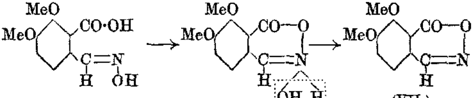
Opianic oxime anhydride is best represented by (II). Of other possibilities, (III) has been excluded by the synthesis of this acid by Hoogewerff and van Dorp (*Rec. trav. chim.*, 1895, **14**, 274), (IV) and (V) are unlikely, since the compound is unaffected by boiling acetic anhydride—a reagent which would acetylate (V) and might be expected to convert (IV) into hemipinimide by a Beckmann change (Brady and Dunn, J., 1926, 2411).

Adopting the new configurations, the formation of the anhydride from the oxime may be represented as a simple ring closure between vicinal groups,



(VI.)

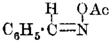
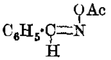
or by a mechanism analogous to that employed by Meisenheimer (*Ber.*, 1924, **57**, 278) to explain the formation of an anhydride from γ-benzildioxime.



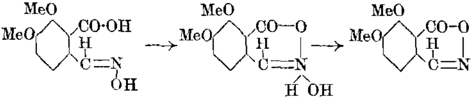
(VII.)

We prefer the second mechanism, because opianic oxime anhydride behaves as the acyl derivative of a β-aldoxime, giving the nitrile (III) and not the original oxime on warming with alkalis. Since opianic oxime is an α-aldoxime, during anhydride formation a change of configuration must have taken place. This occurs only if the second mechanism be adopted, (VI) representing an acyl derivative of an α-aldoxime (compare acetyl-α-benzaldoxime, VIII), and (VII)

an acyl derivative of a β-aldoxime (compare acetyl-β-benzaldoxime, IX).

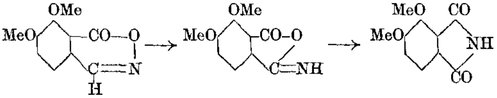
(VIII.)   (IX.)

If Hantzsch's configurations of the aldoximes be adopted, in order that a change of configuration shall take place during anhydride formation, the constitution (VI) must be assigned to the anhydride. Such a structure seems improbable on account of the difficulty of translating it into a spatial formula.

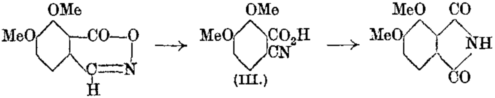

(VI.)

The behaviour of opianic oxime anhydride accordingly supports the new configuration of the aldoximes.

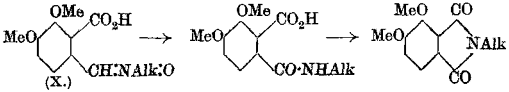
The *formation of hemipinimide from opianic oxime anhydride* may be regarded as taking place either through a *trans*-Beckmann change,



or through the intermediate formation of 2-cyano-5 : 6-dimethoxybenzoic acid (III), which has been shown to give hemipinimide on heating (Hoogewerff and van Dorp, *loc. cit.*).

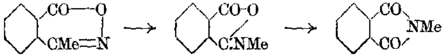

(III.)

The chief argument in favour of the former is that we have found that the *N*-alkyl derivatives of opianic oxime (X) on fusing, on


(X.)

heating in solvents in the presence of acids, or on boiling with acetic anhydride, give alkyl hemipinimides. Here there is no possibility

of nitrile formation and the reaction is best interpreted as a Beckmann change (compare also the change of the oxime of lævulic acid to *N*-methylsuccinimide; Bredt and Böddinghaus, *Annalen*, 1889, **251**, 316). On the other hand, in favour of the cyano-acid mechanism the following considerations can be urged. Allendorff (*Ber.*, 1891, **24**, 2347) was able to isolate *o*-cyanobenzoic acid as an intermediate product in the conversion of the analogous phthalaldehydic oxime anhydride into phthalimide by heat. The isolation of the cyano-acid in the case of opianic oxime anhydride could not be expected, for, whereas *o*-cyanobenzoic acid changes to phthalimide at a temperature above the melting and transition point of the oxime anhydride, 2-cyano-5 : 6-dimethoxybenzoic acid changes to hemipinimide at a temperature at which opianic oxime anhydride is stable. Opianic oxime anhydride does not contain a quinquevalent nitrogen atom, the presence of which Brady and Dunn (*loc. cit.*) regard as necessary before the Beckmann change can occur. Finally we have found that the anhydride of the oxime of acetophenone-*o*-carboxylic acid (Gabriel, *Ber.*, 1883, **16**, 1995) is unaltered on melting, can be distilled unchanged under reduced pressure, and is not affected by heating for 10 minutes at 100° with concentrated sulphuric acid. Nitrile formation cannot occur in this case, but a Beckmann change should give *N*-methylphthalimide.



It seems, therefore, that the cyano-acid must be the intermediate stage in the change of opianic oxime anhydride to hemipinimide.

The action of methyl sulphate upon an alkaline solution of opianic oxime or of *O*-methylhydroxylamine upon opianic acid leads to the formation of *O*-methylopianic oxime, a stable compound unchanged on fusion.

We have measured the absorption spectra of opianic oxime, its anhydride, and *O*- and *N*-methyl ethers and those of hemipinimide and *N*-methylhemipinimide (Fig. 1). The curves for the oxime and the *O*- and *N*-ethers are normal (compare Brady, J., 1914, **105**, 2111), but the curve for the anhydride differs widely from those usually obtained for acylated aldoximes (Brady and Grayson, unpublished work) and suggests a relationship between the anhydride and hemipinimide which is not borne out by their chemical properties. The curves, however, cannot be said to throw much further light on the constitution of the compounds.

In connexion with this work the possibility of an analogo reaction between hydroxylamine and 4-nitrobenzaldehyde

sulphonic acid has been investigated, but no indication of the formation of the expected 4-nitrosaccharin was obtained even on heating the aldehyde with aqueous hydroxylamine hydrochloride at 160°.

The two forms, white and yellow, of phthaloxime (Lassar-Cohn, *Annalen*, 1880, **205**, 295; Lach, *Ber.*, 1883, **16**, 1781; Pratt and Orndorff, *Amer. Chem. J.*, 1912, **47**, 89) have been re-investigated.

FIG. 1.

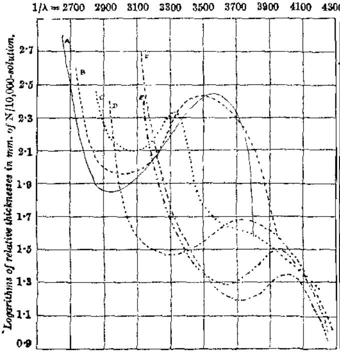
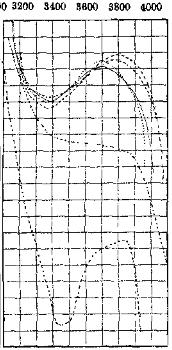


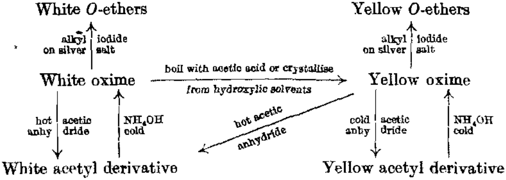
FIG. 2.



A = *Methylhemipinimide.* B = *Hemipinimide.* C = *Opianic oxime anhydride.* D = N-*Methylopianic oxime.* E = O-*Methylopianic oxime.* F = *Opianic oxime.*

——— *Yellow Phthaloxime.* .... *White Phthaloxime.* - - - - - - - - *Yellow O-Methylphthaloxime.* - - - - - - *White O-Methylphthaloxime.* · · · · · · · · · N-*Methylphthaloxime.* - - - - - - - - *Phthalimide.*

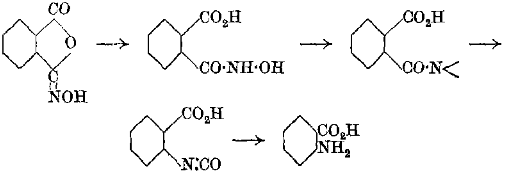
Both forms melt and decompose at the same temperature and both yield series of derivatives in which the characteristic difference in colour persists. The various reactions may be summarised thus:



Analogous derivatives of the white and the yellow oxime always melt at the same temperature and the white and the yellow form show no depression of melting point in admixture. Both oximes give deeply coloured alkali salts, from which the original oximes are reprecipitated by acids. Pratt and Gibbs (*Philippine J. Sci.*, 1913, **8**, 165) measured the absorption spectra of the two phthaloximes and of a number of their derivatives and also those of phthalimide, phthalanil, and related compounds. From their curves, which agree very closely with those obtained by us (Fig. 2), and from the other reactions of the phthaloximes they concluded that these compounds are stereoisomerides. Pratt and Orndorff assumed that the ethers they obtained were both *O*-ethers, and we have now established this in the case of the methyl ethers by the quantitative formation of methyl iodide on boiling them with hydriodic acid and by the production of *O*-methylhydroxylamine by hydrolysis. By methylating a suspension of the sodium salts in methyl alcohol with either methyl iodide or methyl sulphate, only the *O*-ethers were obtained, no *N*-methyl derivative being formed. However, an *N*-methyl compound has been prepared from phthalic anhydride by the action of *N*-methylhydroxylamine; this compound was white and we were unable to prepare a yellow modification under any conditions. The absorption spectra of the two oximes of the sodium salts and *O*-methyl ethers have been reinvestigated and that of the new *N*-ether has been determined. It was noticed that the derivatives of the yellow phthaloxime fluoresce green when their solutions in absolute alcohol are exposed to light from a tungsten arc, and that the yellow oxime, the white oxime, and its derivatives do not. The close similarity of the absorption spectra and the identity of melting points of the two forms rule out the possibility of one having the hydroxyimide structure $C_6H_4(CO)_2$:N·OH and differentiate the compounds from chromoisomerides. Polymorphism is excluded by the differential action of light on solutions of the two forms and by the fact that the solutions of the white or yellow oximes in alkali regenerate the parent compounds on acidification. Whilst it is true that the absorption spectra of the two forms differ by about the same amount as do those of α- and β-aldoximes, there is no evidence otherwise that they are stereoisomerides in the ordinary sense. The stereoisomeric oximes usually differ considerably in melting point and give normal fusion curves when mixed. The phthaloximes, in their chemical reactions, behave identically and, in spite of special attention, no indication has been obtained of those differences in chemical behaviour which distinguish stereoisomerides. We believe, therefore, that the phthaloximes exhibit a special type of

isomerism for which an explanation has still to be found and of which numerous examples are now accumulating (compare the white and the yellow form of diphthalyl-2 : 7-naphthylenediamine, Kuhn, Jacob, and Fürter, *Annalen*, 1927, **455**, 256, and also the work of Heller, *Ber.*, 1925, **58**, 838; 1927, **60**, 909). We believe that the white and the yellow forms of some carbanilino-derivatives of the oximes (Goldschmidt and van Rietschoten, *Ber.*, 1893, **26**, 2089; Brady and Thomas, J., 1922, **121**, 2100) and the white and the yellow form of *iso*nitrosomalonmono-*p*-tolylamide (Plowman and Whiteley, J., 1924, **125**, 590) also exhibit this new type of isomerism, which may perhaps be called xanthoisomerism.

Lassar-Cohn obtained anthranilic acid from the white phthaloxime by the action of one equivalent of boiling alcoholic potassium hydroxide, hut was unable to repeat this result. We were likewise unsuccessful under these conditions, but obtained small yields of anthranilic acid from both white and yellow oximes by using a higher temperature and amyl-alcoholic potassium hydroxide. The change is probably an example of the Hofmann reaction :



Experimental.

Action of Acetic Anhydride on Opianic Oxime.—Opianic oxime was prepared by Perkin's method (*loc. cit.*), 30% potassium hydroxide solution being used in place of the dilute alkali recommended by him, since this gives much better results. The oxime dissolved when treated with the minimum amount of acetic anhydride at room temperature, but no acetyl derivative separated on cooling to −20°; opianic oxime anhydride crystallised when the solution was poured into ice-cold water.

Action of 2 : 4-Dinitrochlorobenzene on Opianic Oxime.—The oxime (3 g.) was dissolved in alcohol, and a solution of sodium ethoxide (sodium, 0·7 g., in 12 c.c. of alcohol) added; the disodium salt then separated as a white precipitate. To the cooled suspension, 2 : 4-dinitrochlorobenzene (3 g. in 9 c.c. of hot alcohol) was added, the brown solution obtained was kept for an hour, and the preci-

pitate was then collected and washed first with a little alcohol and then thoroughly with water to remove sodium chloride. On crystallising from alcohol, it gave 2 : 4-*dinitrophenylopianic oxime* as bright yellow needles, m. p. 146° (Found: N, 11·0. $C_{16}H_{13}O_9N_3$ requires N, 10·7%).* Hydrolysis by heating in the water-bath for 5 hours with 6*N*-sodium hydroxide gave sodium dinitrophenoxide, but hemipinic acid could not be isolated from the rather tarry alkaline solution.

Action of Alkalis on Opianic Oxime Anhydride.—To a warm solution of potassium hydroxide (10 g.) in water (50 c.c.), opianic oxime anhydride (2·6 g.) was added with mechanical stirring; it dissolved to a pale yellow solution. In order to detect opianic oxime, methyl sulphate (4 c.c.) was added and the stirring continued for 2½ hours. The solution was cooled in ice and concentrated hydrochloric acid (15 c.c.) added slowly; an oil separated which soon solidified and after drying in a desiccator formed a sandy powder (0·95 g.), m. p. 74—80°, resolidifying immediately to hemipinimide. In all its properties this compound was identical with the 2-cyano-5 : 6-dimethoxybenzoic acid described by Hoogewerff and van Dorp (*loc. cit.*).

When the reaction was carried out at 0°, uncrystallisable sticky solids were obtained from which only hemipinimide could be isolated. No trace of *O*-methylopianic oxime was detected in any experiment.

The anhydride (1 g.) was dissolved in a solution of sodium ethoxide (sodium, 0·23 g., in 20 c.c. of hot alcohol) and 2 : 4-dinitrochlorobenzene (1 g. in 5 c.c. of hot alcohol) added. No 2 : 4-dinitrophenylopianic oxime separated, but after 3 days dinitrophenetole crystallised, this being formed by the action of the alkali and alcohol on the dinitrochlorobenzene.

N-*Methylopianic Oxime.*—A solution of opianic acid (5 g.) in potassium hydroxide (5·5 g. in 50 c.c. of water) was cooled and to it was added a concentrated aqueous solution of *N*-methylhydroxylamine hydrochloride (3 g.). The mixture was kept at room temperature for 12 hours, 2*N*-hydrochloric acid (32 c.c.) was then added, and the precipitate produced was crystallised from dilute alcohol, N-*methylopianic oxime* being obtained as colourless prisms, m. p. 180·5° (decomp.) (Found: N, 5·9. $C_{11}H_{13}O_5N$ requires N, 5·9%).

N-Methylhemipinimide.—*N*-Methylopianic oxime (5 g.) was boiled with water (100 c.c.) under reflux for 3 hours. After cooling, a small quantity of *N*-methylhemipinimide slowly crystallised.

* In the determination of nitrogen in opianic acid derivatives by Dumas' method, cuprous chloride must be mixed with the copper oxide to prevent the formation of methane.

The mother-liquor on evaporation to small bulk yielded some crystals of unchanged *N*-methylopianic oxime; these were removed and the filtrate was warmed with 2*N*-sodium hydroxide, methylamine and sodium hemipinate being produced. The main product of the reaction was apparently the soluble methylamine hydrogen salt of hemipinic acid; Liebermann (*loc. cit.*) obtained ammonium hydrogen hemipinate similarly from opianic oxime anhydride. No compound analogous to the anhydride of the oxime was obtained either in this experiment or when opianic acid (6 g.) in alcohol (18 c.c.) was shaken with *N*-methylhydroxylamine hydrochloride (2·9 g.) for 45 minutes (compare Liebermann, *loc. cit.*). The acid dissolved and *N*-methylopianic oxime soon crystallised; the alcoholic solution on evaporation gave only ψ-opianic ester (Anderson, *Annalen*, 1853, **86**, 194).

When *N*-methylopianic oxime was heated for 10 minutes at 180° in an evaporating basin, some ebullition occurred just above the melting point. The intramolecular change, however, proceeded without the violence that characterises the change of opianic oxime to hemipinimide. After cooling, the product was stirred with a little alcohol, and the solid crystallised three times from alcohol, pure *N*-methylhemipinimide being obtained.

Opianic acid (5 g.) and *N*-methylhydroxylamine hydrochloride (1·7 g.) were heated together under reflux for 3 hours with 80% alcohol (30 c.c.). On cooling, a solid separated which gave pure *N*-methylhemipinimide after one crystallisation from alcohol.

Hemipinimide (2·5 g.), prepared by boiling opianic acid in alcoholic solution with hydroxylamine hydrochloride, was dissolved in hot dry amyl alcohol, and a solution of potassium (0·75 g.) in dry amyl alcohol added; after cooling, the solid was collected, washed with dry ether, and quickly transferred to a desiccator containing solid sodium hydroxide. The yield of potassium hemipinimide was almost quantitative (compare Hammick and Locket, J., 1922, **121**, 2362). The salt was heated with excess of methyl iodide for 5 hours in a sealed tube at 150°; the solid obtained gave *N*-methylhemipinimide, m. p. 168°, after two crystallisations from alcohol. Freund and Heim (*Ber.*, 1890, **23**, 2905) obtained this compound by the action of dilute nitric acid on the methylamide of methylhydrastinine.

O-*Methylopianic Oxime*.—Opianic acid (5 g.) was dissolved in 2*N*-sodium hydroxide (30 c.c.), a solution of *O*-methylhydroxylamine hydrochloride (2·2 g. in 25 c.c. of water) added, and the mixture kept in a closed bottle for 12 hours. Addition of dilute hydrochloric acid then precipitated O-*methylopianic oxime*, which crystallised from benzene and light petroleum or from chloroform

in colourless cubes, m. p. 112° (Found: N, 6·3. $C_{11}H_{13}O_5N$ requires N, 5·9%).

Opianic acid (5 g.) was dissolved in 4*N*-potassium hydroxide (100 c.c.), and a concentrated aqueous solution of hydroxylamine hydrochloride (2·5 g.) added slowly. To the cold solution, methyl sulphate (10 g.) was added cautiously with cooling and shaking. The mixture was kept for 2 hours, and a slight excess of dilute hydrochloric acid added; *O*-methylopianic oxime then separated in good yield. It was purified as before.

N-*Benzylopianic Oxime.*—This was prepared from opianic acid and *N*-benzylhydroxylamine hydrochloride in exactly the same way as *N*-methylopianic oxime (compare Scheiber, *Ber.*, 1911, **44**, 762). On heating it for 6 hours in alcoholic solution with a trace of hydrochloric acid, *N*-benzylhemipinimide (van der Meulen, *Rec. trav. chim.*, 1896, **15**, 282) was obtained. This compound was also formed by heating opianic acid with *N*-benzylhydroxylamine hydrochloride in alcoholic solution.

Methylation of the Sodium Salts of the Phthaloximes.—The white and the yellow methyl ether described by Pratt and Orndorff were prepared by their method from the corresponding silver salts of the oximes. These authors experienced difficulty in alkylating the sodium salts, but we have been successful with both methyl iodide and methyl sulphate; care, however, must be taken to avoid excess of alkali, which readily decomposes the oximes to hydroxylamine and phthalic acid.

The yellow phthaloxime (2·50 g.) was dissolved in the minimum amount of methyl alcohol, and the red sodium salt precipitated by the addition of sodium methoxide (sodium, 0·35 g., in methyl alcohol). Methyl iodide (2·5 c.c.) was added to the suspension, and the mixture kept in a closed flask for 5 days; the red sodium salt had then disappeared and the liquid was clear orange-yellow. The solution was evaporated at room temperature, and the residue extracted with boiling light petroleum; on cooling, crystals of the yellow *O*-methyl ether of phthaloxime were obtained identical with those obtained from the silver salt (Found: OMe, 17·4. Calc.: OMe, 17·5%). Similarly, from the white phthaloxime the white *O*-methyl ether of phthaloxime was obtained identical with that prepared from the silver salt (Found: OMe, 17·3%).

A solution of white phthaloxime (5·02 g.) in methyl alcohol (75 c.c.) was treated with sodium methoxide (0·71 g. of sodium in the minimum amount of methyl alcohol), and methyl sulphate (5·6 c.c.) added. The mixture was kept for 1¾ hours with occasional shaking, the reaction then being complete. After 45 c.c. of the solvent had been removed in a vacuum, and the remainder cooled, a mixture of the

white *O*-methyl ether and sodium sulphate separated, from which the ether was extracted with chloroform; the filtrate on concentration yielded more *O*-ether. Similarly, the yellow oxime gave the yellow *O*-ether. In all these methylations the addition of a little water greatly increases the reaction velocity without, however, much affecting the yield, which was never more than 25%. Although a careful search was made, in no case was any trace of an *N*-methyl derivative detected.

Hydrolysis of O-*Methylphthaloxime*.—White *O*-methylphthaloxime (9·8 g.), dissolved in 2*N*-sodium hydroxide (80 c.c.), was heated on the water-bath for an hour and the solution was then acidified with hydrochloric acid and cooled. The precipitated phthalic acid was removed, and the solution evaporated to dryness on the water-bath. The residue was washed with ether to remove phthalic acid and extracted twice with small quantities of hot absolute alcohol; on cooling, and addition of ether to the combined extracts, *O*-methylhydroxylamine hydrochloride (m. p. 149—151°) was precipitated. It was further identified by conversion into α-*O*-methyl-*m*-nitrobenzaldoxime.

N-*Methylphthaloxime*.—A solution of *N*-methylhydroxylamine hydrochloride (9 g. in 9 c.c. of water) and sodium carbonate (5·7 g. in 160 c.c. of water) was heated to 60°, finely powdered phthalic anhydride (12·7 g.) slowly stirred in, and the solution kept at 60° for 1½ hours. A white, crystalline precipitate separated which after crystallisation from alcohol gave N-*methylphthaloxime* as colourless crystals, m. p. 121—122° (Found: N, 7·9. $C_9H_7O_3N$ requires N, 7·9%). This compound, on boiling for a short time with hydrochloric acid, gave phthalic acid and *N*-methylhydroxylamine. Boiling with concentrated hydriodic acid gave methylamine, which was identified by Valton's method (J., 1925, **127**, 40). Variations in the experimental procedure failed to yield a yellow form.

Action of Potassium Hydroxide on the Phthaloximes.—White or yellow phthaloxime (5·4 g.) in amyl alcohol (180 c.c.) was treated with one equivalent of potassium hydroxide (1·86 g.) in water (12 c.c.), and the mixture boiled under reflux for 2 hours; the red colour of the potassium salt had then changed to clear yellow. Most of the solvent was removed in a vacuum, and the solid, which separated on cooling, was collected and dissolved in the minimum amount of hot water; on just acidifying the solution with acetic acid and cooling, anthranilic acid separated; it was obtained pure after one crystallisation from hot water.

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LXIX.—*Studies on Hydrogen Cyanide. Part I. Mercuric Methyl Cyanide and the Alleged Isomerides of Hydrogen Cyanide.*

By Joseph Edward Coates, Leonard Eric Hinkel, and Thomas Huber Angel.

Enklaar (*Rec. trav. chim.*, 1923, **42**, 1000; 1925, **44**, 889; 1926, **45**, 414), having on the basis of the Drude theory developed a theory of optical dispersion in which dispersion electrons are correlated with valency electrons, and having measured the dispersion of hydrogen cyanide, nitriles, and carbylamines, found evidence for the view that hydrogen cyanide behaves optically as a 50% mixture of HCN and HNC, or as though the hydrogen atom were bound equally to the atoms of carbon and nitrogen. Nevertheless, he regards as improbable the view that ordinary hydrogen cyanide consists of a 50% mixture of isomerides, since he claims to have isolated these isomerides as separate individuals and to have shown that one of them (considered to be HNC) is stable and the other, HCN, unstable. In view of its importance in connexion with the problem of the constitution of hydrogen cyanide, it seemed desirable to repeat the experiments upon which this claim was based.

Enklaar recognised the isomerides solely by their reaction with mercuric methyl hydroxide, in which two mercuric methyl cyanides of different melting points were formed, *viz.*, that melting at 90·5°, regarded as the derivative of the stable acid HNC, and that melting at 60°, corresponding to the "labile" acid HCN. Gaseous hydrogen cyanide generated by various simple reactions is said to yield in some cases the former, in others the latter derivative, thus indicating the separate existence of two isomeric forms of the gas. Further, the derivative of lower melting point is obtained from the reaction between mercuric methyl iodide and silver cyanide, and also by the spontaneous transformation of the form melting at the higher temperature when it is kept for several months at about 6°.

The Alleged Isomerides of Hydrogen Cyanide.—Enklaar found that (*a*) silver cyanide, alone or, better, in potassium cyanide solution, and (*b*) a solution of mercuric cyanide, when slightly decomposed by a small quantity of hydrogen sulphide yielded gaseous hydrogen cyanide, which, when led directly into aqueous mercuric methyl hydroxide, always gave the derivative of low melting point. In a later paper (*loc. cit.*, 1925), however, he reports a product similarly me[illegible]ined as melting at 89·5°, without remarking on the inconsistency. the for[illegible]

He also found that the hydrogen cyanide first evolved from an acidified solution of sodium ferrocyanide is "stable" (yielding the high-melting derivative), whereas that evolved after a few minutes' boiling is "labile" (yielding the low-melting derivative). Again, the hydrogen cyanide distilled from acidified solutions of potassium cyanide was unaccountably sometimes stable, sometimes labile, yielding a mercuric methyl cyanide melting as often at the higher as at the lower temperature. The claim is also made that the derivative obtained by distilling hydrogen cyanide from a system that is not free from water has a slightly lower melting point than that of the derivative produced by hydrogen cyanide distilled from an anhydrous system, the presence of water thus causing a certain amount of conversion of the stable into the labile acid. No attention is directed to a contradiction of this in the same paper (*loc. cit.*, 1925).

A repetition of these experiments has shown that mercuric methyl cyanide, produced directly from the pure base and hydrogen cyanide (whatever its origin), invariably melts, not at 90·5°, but at 93° without further purification, and the same substance obtained from mercuric methyl iodide and silver cyanide melts at 93° after purification. In a careful study of this substance no evidence has been found for the separate existence of a form melting at 60°. It suffers no change on keeping.

The variation in melting point of Enklaar's derivatives might be due to the use of impure substances. He employed mercuric methyl hydroxide melting at various temperatures between 92° and 97°. The pure base melts at 106°, cannot be purified from alcohol as attempted by Enklaar, and decomposes fairly rapidly on keeping; also it detonates when subjected to analysis by the ordinary combustion method (Hinkel and Angel, J., 1927, 1948), but Enklaar appears to have found no such difficulty. The melting point of mercuric methyl cyanide is greatly influenced by the presence of traces of moisture or solvents.

It might be objected that the processes of purification of the mercuric methyl cyanide obtained from the iodide and silver cyanide (the product from pure acid and pure base needed no purification) could convert any low-melting derivative into the high-melting form, and that Enklaar was right in avoiding purification. But when impurity is likely to be present (probably mercuric methyl iodide) no valid conclusions can be drawn from the melting point. Further, by this reaction an initial unpurified product could be obtained having a melting point only a few degrees below that of the pure high-melting derivative.

EXPERIMENTAL.

For the preparation of mercuric methyl cyanide directly from base and acid, the hydrogen cyanide was obtained, not only by the reactions referred to above, but also from a stock of the pure anhydrous substance prepared by dropping a concentrated solution of sodium cyanide into 65% sulphuric acid, the distillate being dehydrated by treatment with anhydrous sodium sulphate, followed by repeated distillation and treatment with phosphorus pentoxide extending over many months. Its boiling point was 25·7°/760 mm.

The mercuric methyl iodide employed melted at 145° and the hydroxide at 106°. Both were prepared and purified as described by Hinkel and Angel (*loc. cit.*).

Preparation of Mercuric Methyl Cyanide.—5 G. of mercuric methyl iodide in 25 c.c. of absolute alcohol were shaken at room temperature for 3 hours with 2·1 g. (a slight excess) of powdered silver cyanide. After the silver iodide and silver cyanide had been separated and the alcohol evaporated in a vacuum, white crystals remained, melting (not sharply) at 85°. (Enklaar, who gives no details, obtained by this method a product melting a little above 60°, rarely lower, which he considered to be the isomeride of the compound of higher melting point.) The product, after being twice dissolved in the minimum amount of boiling ether and precipitated by the gradual addition of light petroleum (b. p. 40—60°), and dried in a vacuum, melted sharply at 93°. A repetition of this process, using instead of ethyl alcohol (*a*) ether dried by sodium, (*b*) methyl alcohol, gave a product melting at 93° after purification. A preparation in the presence of a large excess of silver cyanide melted without any purification at 89° (after previous softening). The impurity is probably mercuric methyl iodide.

The preparation was also carried out by the use of a slight excess of mercuric methyl iodide, the mixture being boiled for 2 hours. The mercuric methyl iodide was separated by treatment with boiling water, in which it is practically insoluble. After purification as before, the product melted at 93° (Found : N, by Kjeldahl method, 5·75. C_2H_3NHg requires N, 5·78%).

The Properties of Mercuric Methyl Cyanide.—The only information in the literature on this substance is that given by Enklaar. The substance is readily soluble in water, methyl or ethyl alcohol, anhydrous hydrogen cyanide, and benzene, and fairly readily soluble in ether, from which it may be precipitated by the addition of light petroleum (b. p. 40—60°). It crystallises in colourless, lustrous, acicular plates with a faint smell of garlic, somewhat resembling that of the base. No change of melting point occurs (1) after heating the

melt at 100° for several minutes, (2) after keeping at 0° for several days, and (3) after keeping at room temperature for 9 months. This may be contrasted with Enklaar's statement that the compound of higher melting point, on keeping for several months at about 6°, changes largely into the form of lower melting point.

The aqueous solution resembles that of mercuric cyanide in being neutral to indicators even after boiling for 10 minutes (compare other mercuric methyl salts, Maynard and Howard, J., 1923, **123**, 960). The behaviour of mercuric methyl cyanide with methyl iodide is precisely similar to that of mercuric cyanide and silver cyanide, a double compound being first formed which breaks down into methyl carbylamine at a higher temperature. With dry hydrogen chloride, mercuric methyl cyanide, dissolved in dry ether, slowly forms white crystals of mercuric methyl chloride. In aqueous solution hydrochloric acid precipitates the same substance, silver nitrate precipitates silver cyanide, and hydrogen sulphide mercuric methyl sulphide. Caustic potash, ammonia, and potassium iodide give no apparent reaction. Dilute sulphuric acid readily liberates hydrogen cyanide (according to Enklaar, this does not occur).

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LXX.—*Acid and Salt Effects in Catalysed Reactions. Part XII. The Water Catenary* (H^+–H_2O–OH^-) *in the Iodination of Acetone.*

By HARRY MEDFORTH DAWSON and ARTHUR KEY.

SINCE the publication of the first of this series of papers (Dawson and Carter, J., 1926, 2282), in which evidence was brought forward to show that catalytic effects are produced by negatively charged anions and by electrically neutral molecules as well as by positively charged "hydrogen" (oxonium) ions, the existence of similar effects has been conclusively demonstrated in other catalysed reactions. Studies of the mutarotation of glucose by Brönsted and Guggenheim (*J. Amer. Chem. Soc.*, 1927, **49**, 2554) and by Lowry and Smith (J., 1927, 2539) have established the activity of anions and molecules in this reaction, and have also shown that catalytic activity must be attributed to other complex positive ions of the oxonium type, such as $NH_4^{\cdot}$, $NH_3R^{\cdot}$, etc. It seems probable that the activity of all such ions and molecules depends on their acid

or basic character, that is to say, on their ability to act as proton donators or proton acceptors.

From an examination of the data for a large number of hydrolytic reactions, Skrabal (*Z. Elektrochem.*, 1927, **33**, 322) concludes that the very wide differences which are exhibited by such reactions towards changes in the concentration of the hydrogen ion can be satisfactorily interpreted in terms of the joint action of the hydrogen ion, hydroxyl ion, and undissociated water when the large variations in the relative values of the respective catalytic coefficients are taken into account. Skrabal has also shown the existence of symmetry in the curve which is obtained by plotting the logarithm of the reaction velocity against p_H. This symmetry is a particular and necessary consequence of the more general relations which have been shown by one of us to apply to the catalytic effects produced by any weak acid in virtue of the activity of the positive ions, negative ions, and undissociated molecules.

For acid–salt mixtures of the type cHA + xMA, where c is constant and x is variable, the plot of the reaction velocity against the logarithm of the hydrogen-ion concentration or p_H gives a catenary curve. The salt-free solution of the acid represents the limiting member of such a series of mixtures, but the catenary curve is not actually limited by this circumstance, for the addition of a completely ionised acid in which the hydrogen ion is associated with a catalytically inert anion, should obviously be equivalent to the addition of the salt MA, in which the active anion is associated with a catalytically inert metallic cation. The symbol $(H^+–HA–A^-)_c$ may be conveniently used when reference has to be made to the catenary curve which corresponds with the acid HA at the concentration represented by c. If the acid in question is water, the catalytic effects correspond with the water catenary, $H^+–H_2O–OH^-$.

The usual conditions under which catalytic observations are made with the strong acids and bases correspond with the upper reaches of the water catenary, and the data so obtained may be taken as an accurate measure of the catalytic activity of the hydrogen ion or of the hydroxyl ion if the activity of the undissociated water is negligibly small. When, however, the catalysed reaction involves the formation or disappearance of acid or basic substances, the changes thereby produced in the hydrogen-ion concentration are such as to prevent the realisation of those conditions which are essential for the direct investigation of the lower portion of the water catenary. Constancy of p_H may be obtained by the use of buffer solutions, and it has been shown (*J.*, 1927, 1290) that the velocity which is characteristic of the minimum-velocity (*M.V.*) point on the water catenary may be derived indirectly from the

minimum velocity which is shown by series of buffer mixtures for which the concentration of the buffer acid or the concentration of the buffer salt is constant. In the application of this method, it is, however, necessary to know the values of the catalytic coefficients for both the undissociated acid and the acid anion in the buffer mixture.

In the present paper, an alternative method of procedure is described which has the advantage of great simplicity, and furthermore permits of the determination of the velocity which is characteristic of any desired point on the water catenary. This velocity is given by the equation

$$v_0 = v_h + v_{OH} + v_w = k_h[H^+] + k_{OH}[OH^-] + k_w[H_2O] \quad . \quad (1)$$

or since $[H^+].[OH^-] = K_w$ and $[H_2O] = 55$

$$v_0 = k_h[H^+] + k_{OH}K_w/[H^+] + 55k_w \quad . \quad . \quad . \quad (1a)$$

according to which the velocity is determined by the hydrogen-ion concentration. If this hydrogen-ion concentration is produced by the use of a buffer mixture cHA + sMA, in which the ratio c/s is constant = q, the value of $[H^+]$ is given by

$$[H^+] = K(c - [H^+])/(s + [H^+]),$$

and if c and s are not too small, this is equal to Kq. For such a buffered solution, the reaction velocity is given by

$$v = k_h[H^+] + k_{OH}[OH^-] + k_w[H_2O] + k_mc + k_as$$
$$= v_0 + k_mc + k_as \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which may be written in the form

$$v = v_0 + (k_a + qk_m)s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

or

$$v = v_0 + (k_m + k_a/q)c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2b)$$

according to which the velocity is a linear function of the concentration of the salt or the acid in the buffer mixtures. When the straight line for a series of buffers with a fixed value of q is extrapolated to zero salt (or acid) concentration, we obtain the velocity v_0 which is characteristic of the isohydric point on the water catenary, and by variation of q it is possible to derive the velocities for a series of points on this catenary. In the application of this method it is by no means necessary to confine the buffer solutions to those derived from the same acid. In practice, the choice of buffer will depend on the hydrogen-ion concentration of the *M.V.* point of the water catenary, and this will vary with the nature of the catalysed reaction. When acidic or basic substances are produced in the reaction, the value of q should not be greater than, say, 10, nor less than about 0·1. Variations of q between these

limits give a range of hydrogen-ion concentrations which i represented by a difference of 2·0 units on the p_H scale.

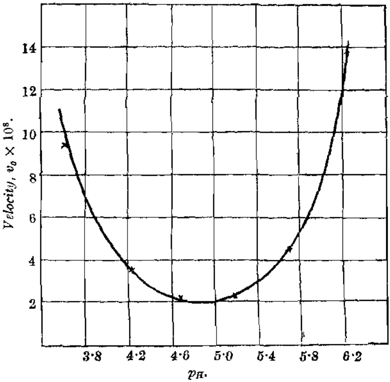
The experiments to be described have reference to the catalyti effects observed with isohydric series of buffers in the reactioi between acetone and iodine. Acetate buffers were usually employed and for these the hydrogen-ion concentration was derived fron $K = 1 \cdot 85 \times 10^{-5}$. For the lowest hydrogen-ion concentration, a phosphate buffer was used, and it is necessary to consider th co-ordination of this with the acetate buffers. The measurement which permit of the derivation of a value for the second-stag dissociation constant K_2 of phosphoric acid have been recentl examined by Prideaux and Ward (J., 1924, **125**, 423). It appear that the "constant" obtained for mixtures of $NaH_2PO_4 + Na_2HPO$ increases with the total concentration and also with the proportioi of the disodium salt. The measurements which relate most nearl to the conditions in our experiments are those of Michaelis and Krüger (*Biochem. Z.*, 1921, **119**, 307), and in accordance with thei results the value $1 \cdot 1 \times 10^{-7}$ has been adopted for K_2 in the deriv ation of the hydrogen-ion concentration.

When the observed reaction velocities for each series of isohydri solutions are plotted against the concentration of the buffer con stituents, the points are found to lie very closely on straight lines a required by equations (2*a*) and (2*b*). If the extrapolated values o v_0 are then plotted against the logarithm of the hydrogen-ion con centration (see Fig. 1), a catenary curve is obtained which i symmetrical with respect to the point for which $p_H = 4 \cdot 90$, o $[H^+]_i = 1 \cdot 25 \times 10^{-5}$. This is the *M.V.* point on the water catenary and the magnitude of the velocity v_i according to this curve (see Fig. 1) is about $0 \cdot 019 \times 10^{-6}$ mols. per litre per minute. This velocity refers to 25° and an acetone concentration of 20 c.c. per litre.

In accordance with the relations which have been shown to hold at the *M.V.* or isocatalytic point, the minimum value of the velocity due to the joint action of the hydrogen and hydroxyl ions shoulc be given by $u_i = 2k_h[H^+]_i$. When $k_h = 4 \cdot 65 \times 10^{-4}$ and $[H^+]_i = 1 \cdot 25 \times 10^{-5}$ are substituted in this equation, we obtain $u_i = 0 \cdot 012 \times 10^{-6}$. This is clearly much lower than the minimum velocity $v_i = 0 \cdot 019 \times 10^{-6}$ which is indicated by the experiments with the buffer solutions, and it would seem fairly obvious that the difference is to be attributed to the catalytic action of undissociated water. In other words, the difference corresponds with $v_w = k_w[H_2O] = 0 \cdot 007 \times 10^{-6}$. In previous measurements of the catalytic effects which are produced by mixtures of acetic acid and sodium acetate in the series represented by $0 \cdot 1N\text{-}CH_3 \cdot CO_2H + xCH_3 \cdot CO_2Na$, the

experimental data afforded no evidence of the catalytic activity of the water molecules, but the reason for this is obviously to be found in the very small magnitude of the water effect. Since the minimum velocity for the above constant-acid series is about $0{\cdot}3 \times 10^{-6}$, it is evident that the proportion of the total catalytic effect due to the water molecules is only about 2% at the *M.V.* point. For other mixtures of the series the proportion will, of course, be still smaller.

FIG. 1.



Velocity of the acetone–iodine reaction (due to the joint action of hydrogen ions, hydroxyl ions, and water molecules) plotted against p_H.

In order to compare the experimental values of v_0 with those given by equation (2), it is necessary to know the value of the coefficient k_{OH}. The difficulties associated with the determination of this have been referred to in previous papers. A preliminary estimate of $k_{OH} = 10$ was made by Dawson and Carter (*loc. cit.*) on the basis of the velocity data afforded by experiments with acid–salt mixtures belonging to the series $(0{\cdot}2 - x)CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$. Subsequently an independent value was derived from an examination of the course followed by the autocatalysed reaction between acetone and iodine (Dawson, J., 1927, 458). It was shown that the early stages of the autocatalytic change were generally consistent with the assumption that the reaction proceeds under the joint catalytic influence of the hydrogen and hydroxyl

ions as represented by the equation $v = k_h[H^+] + k_{OH}[OH^-]$. The results obtained in the present investigation indicate, however, that this equation should include a term to correspond with the catalytic action of the undissociated water. For the purpose of this inquiry, it will suffice to point out that the introduction of the water term leads to a lower value for k_{OH} than that which was derived on the assumption that the water effect could be neglected, and that the present experiments seem to afford a simpler method for the determination of k_{OH}. This method is based on the equation which expresses the connexion between the hydrogen-ion concentration of the *M.V.* point on the water catenary and the catalytic coefficients k_h and k_{OH}. This equation is $[H^+]_i = \sqrt{k_{OH}K_w/k_h}$, and by substituting $[H^+]_i = 1{\cdot}25 \times 10^{-5}$, $k_h = 4{\cdot}65 \times 10^{-4}$, and $K_w = 10^{-14}$ we obtain $k_{OH} = 7{\cdot}2$. A comparison of the values of v_0 obtained from the experiments with the buffer solutions and those calculated from the equation

$$v_0 = v_h + v_{OH} + v_w = k_h[H^+] + k_{OH}[OH^-] + k_w[H_2O]$$

may now be undertaken. In Table I, the hydrogen-ion concentration is recorded in the first column; cols. 2, 3, 4, and 5 give respectively the values of v_h, v_{OH}, v_w, and v_0; and col. 6 shows the values of v_0 obtained from the buffer solution experiments.

TABLE I.

$[H^+] \cdot 10^5$.	$v_h \cdot 10^6$.	$v_{OH} \cdot 10^6$.	$v_w \cdot 10^6$.	$v_0 \cdot 10^6$ (calc.).	$v_0 \cdot 10^6$ (obs.).
18·5	0·086	0	0·007	0·093	0·092
5·55	0·026	0·001	0·007	0·034	0·034
1·85	0·009	0·004	0·007	0·020	0·022
0·62	0·003	0·011	0·007	0·021	0·022
0·185	0·001	0·038	0·007	0·046	0·044
0·053	0	0·126	0·007	0·133	0·135

The calculated values of v_0 are based on $k_h = 4{\cdot}65 \times 10^{-4}$, $k_{OH} = 7$, and $k_w = 0{\cdot}007 \times 10^{-6}/55 = 1{\cdot}3 \times 10^{-10}$. The ratio between the coefficients for the hydroxyl ion and the water molecule is therefore about 5×10^{10}. The close agreement between the two series of v_0 values would seem to justify the view that the procedure described affords a convenient and trustworthy method for the investigation of the relations which are involved in the joint catalytic action of the hydrogen ion, the hydroxyl ion, and the water molecule.

In so far as the reaction velocities due to the ions are concerned, it has been shown previously (Dawson, J., 1927, 213) that all the catalytic catenaries which correspond with the general formula $(H^+–HA–A^-)_c$ can be replaced by a single catenary. If the hydrogen-ion concentrations and the ionic reaction velocities are expressed in terms of the corresponding values for the respective

isocatalytic or *M.V.* points, such that $n = [H^+]/[H^+]_i$ and $r = u/u_i$, the connexion between the reduced hydrogen-ion concentration (n) and the reduced ionic reaction velocity (r) is given by

$$r = \tfrac{1}{2}(n + 1/n) = \cosh \log_e n,$$

which is the equation of the universal catalytic catenary. By this transformation, the specific catalytic coefficients as well as the ionisation constant and concentration of the catalysing acid are eliminated.

It is of interest to examine the results obtained for the water catenary in reference to the generalised catalytic formula. Since $v_0 = 0{\cdot}019 \times 10^{-6}$ and $v_w = 0{\cdot}007 \times 10^{-6}$, the value of r is given by $u/u_i = (v_0 - v_w)/(v_0 - v_w)_i = (v_0 - 0{\cdot}007 \times 10^{-6})/0{\cdot}012 \times 10^{-6}$, and n by $[H^+]/[H^+]_i = [H^+]/1{\cdot}25 \times 10^{-5}$. In making the comparison between the two sets of values, it should be borne in mind that the values assigned to the very small velocities v_w and u_i and also to $[H^+]_i$ are necessarily only approximate. In Table II, col. 1 gives the hydrogen-ion concentration, col. 2 the reduced hydrogen-ion concentration n, col. 3 the values of $\tfrac{1}{2}(n + 1/n)$, and col. 4 the values of r.

TABLE II.

$[H^+] \cdot 10^5$.	n.	$\tfrac{1}{2}(n + 1/n)$.	r.
18·5	14·8	7·4	7·1
5·55	4·4	2·3	2·35
1·85	1·5	1·1	1·25
0·62	0·50	1·25	1·35
0·185	0·15	3·4	3·1
0·053	0·042	11·9	10·7

Having due regard for the probable degree of accuracy of the data on which the values of r and $\tfrac{1}{2}(n + 1/n)$ are based, the concordance between the two sets of figures is quite good, and it may be claimed that the results obtained in the determination of the water catenary for the acetone–iodine reaction are in agreement with the requirements of the universal catalytic relation $r = \cosh \log_e n$.

EXPERIMENTAL.

The materials used were purified by methods which have been previously described. In all cases, the concentration of the acetone was 20·0 c.c. per litre and the initial concentration of the iodine about 0·001*M*. In order to reduce the disturbing effect of the hydriodic acid, the experiments were conducted on a scale which permitted the use of 100 c.c. samples in the titration of the residual iodine with 0·01*N*-thiosulphate. The hydriodic acid produced during a reaction period which sufficed for the measurement of the velocity was about 0·0001 mol. per litre and the effect of this was

eliminated by the usual method. For each value of p_H, three buffer solutions were used with relative concentrations represented by successive integers. Denoting the integral ratio by m, the velocity for each series may be expressed by $v = v_0 + am$. Such values are shown in the last column of Table III and the close agreement with the observed values in the previous column is an indication of the exactness of the linear relation.

TABLE III.

$[H^+] . 10^5$.	c.	s.	$v . 10^6$ (obs.).	$v . 10^6$ (calc.).
$CH_3 \cdot CO_2H : CH_3 \cdot CO_2Na = 10 : 1$; $v = 0{\cdot}092 + 0{\cdot}096m$.				
18·5	0·05	0·005	0·188	0·188
,,	0·1	0·01	0·283	0·284
,,	0·15	0·015	0·380	0·380
$CH_3 \cdot CO_2H : CH_3 \cdot CO_2Na = 3 : 1$; $v = 0{\cdot}034 + 0{\cdot}044m$.				
5·55	0·015	0·005	0·078	0·078
,,	0·03	0·01	0·123	0·122
,,	0·045	0·015	0·165	0·166
$CH_3 \cdot CO_2H : CH_3 \cdot CO_2Na = 1 : 1$; $v = 0{\cdot}022 + 0{\cdot}026m$.				
1·85	0·005	0·005	0·0485	0·048
,,	0·01	0·01	0·075	0·074
,,	0·015	0·015	0·098	0·100
,,	0·02	0·02	0·127	0·126
$CH_3 \cdot CO_2H . CH_3 \cdot CO_2Na = 1 : 3$; $v = 0{\cdot}022 + 0{\cdot}0625m$.				
0·62	0·005	0·015	0·0835	0·084
,,	0·01	0·03	0·148	0·147
,,	0·015	0·045	0·209	0·210
$CH_3 \cdot CO_2H : CH_3 \cdot CO_2Na = 1 : 10$; $v = 0{\cdot}044 + 0{\cdot}192m$.				
0·185	0·005	0·05	0·236	0·236
,,	0·01	0·10	0·430	0·428
,,	0·015	0·15	0·610	0·620
$NaH_2PO_4 : Na_2HPO_4 = 4{\cdot}80 : 1$; $v = 0{\cdot}135 + 0{\cdot}685m$.				
0·065	$c + s = 0{\cdot}01$		0·82	0·82
,,	,, $= 0{\cdot}02$		1·50	1·50
,,	,, $= 0{\cdot}03$		2·20	2·19

The velocities for the phosphate buffer indicate that catalytic effects of considerable magnitude are brought about by the buffer constituents.

Summary.

Measurements of the rate of the reaction between acetone and iodine in isohydric series of buffer solutions have been used to derive the velocities which are due to the catalytic constituents of water as represented by $v_0 = k_h[H^+] + k_{OH}[OH^-] + k_w[H_2O]$.

The reaction is accelerated by water molecules, although the coefficient k_w is very small. The ratio of k_{OH} to k_w is about 5×10^{10}.

The velocity due to the joint action of the hydrogen and hydroxyl ions is found to be in agreement with the requirements of the generalised catalytic formula $r = \cosh \log_e n$, in which r is the reduced ionic velocity and n the reduced hydrogen-ion concentration.

THE UNIVERSITY, LEEDS. [*Received, January 18th*, 1928.]

LXXI.—*Colloidal Platinum. Part III. Its Natural Acidity and its Coagulation by Acids.*

By STUART W. PENNYCUICK and R. J. BEST.

IN Part II of this series * (Pennycuick, J., 1927, 2600), it was shown that colloidal platinum solutions were definitely acid in nature, behaving more like strong acids than weak acids on titration with bases. It will now be shown (*a*) that the natural acidity of colloidal platinum solutions can be measured with the quinhydrone electrode, (*b*) that the coagulation of platinum sols by different acids takes place at approximately the same p_H, and (*c*) that after coagulation the natural acidity of the solutions still remains.

EXPERIMENTAL.

The p_H *of Pure Platinum Sols.*—The platinum sols were prepared by the method previously described, *viz.*, by sparking pure platinum poles in conductivity water (0·4 gemmho). The p_H values of these sols could not be determined by the hydrogen electrode, owing to far-reaching changes in the nature of the colloid which are now being investigated. The quinhydrone electrode, however, proved entirely satisfactory. It was always used in conjunction with a normal calomel electrode, which was prepared from mercury distilled in a vacuum, potassium chloride thrice crystallised from conductivity water, and calomel prepared according to the authors' method (*Australian J. Exp. Biol. Med. Sci.*, 1926, **3**, 173). The quinhydrone was prepared according to Biilmann and Lund (*Ann. Chim.*, 1921, **16**, 321), and a polished platinum electrode proved superior to one of gold. The electrode vessel, having a total capacity of about 8 c.c., was connected to the middle vessel containing saturated potassium chloride by a glass tube containing 3% agar saturated with the salt. By having one end of this connecting tube reasonably close to the platinum electrode, and by using a highly sensitive galvanometer, readings could be taken to 0·1 millivolt in spite of the high resistance of the sols. (The p_H of the conductivity water used was obtained with the above chain and was approximately 6.) The whole system

* Part I appeared in the *Australian J. Exp. Biol. Med. Sci.*, 1927, **4**, 99.

was sunk in a thermostat at 30°. The various p_H values were calculated from the formula

$$p_H = -\log [H^+] = [(0{\cdot}6953 - 0{\cdot}2835) - E_{obs.}]/0{\cdot}06011.$$

This formula uses the standard value for the normal calomel electrode, *viz.*, 0·2864 at 18°, with a temperature coefficient of − 0·00024/degree, and also the Biilmann and Krarup relation (J., 1924, **125**, 1954) for the quinhydrone electrode, $E_t = 0{\cdot}7175 - 0{\cdot}00074t$.

Before each determination the quinhydrone electrode vessel was washed with conductivity water, air-dried, and subsequently handled only with filter paper; it was twice rinsed with the solution to be used, filled, corked, and placed in the thermostat. Readings were taken as soon as temperature equilibrium had been reached. Great precautions were necessary in order to obtain reproducible values with unbuffered solutions of such dilute acids.

The p_H values were taken for nine different pure platinum sols. They ranged from 4·60 to 4·28, the corresponding hydrogen-ion concentrations being 25×10^{-6} to 52×10^{-6}. The unboiled sols always showed a relatively high p_H and on standing or on boiling in borosilicate vessels showed a marked decrease in p_H; *e.g.*, a freshly prepared unboiled sol showed p_H 4·60; after boiling for 20 minutes this changed to p_H 4·47; and after a further 30 minutes' boiling to p_H 4·30. The acidity as measured by the quinhydrone electrode was always slightly less than that obtained by conductimetric titration, as had been anticipated by Pennycuick (*loc. cit.*). The evidence, however, definitely indicates that the quinhydrone electrode measures the true p_H of these sols, for (*a*) the values obtained are steady and reproducible; (*b*) no anomalies or irregularities appear; and (*c*) on mixing an acid of p_H, say, 4·284, with a platinum sol of the same p_H, the mixture also shows a p_H of 4·284.

The Coagulation of Colloidal Platinum by Acids.—Although the coagulation of colloids by salt solutions has received much attention, relatively little attention has been paid to the coagulation by acids. Tartar and Gailey (*J. Amer. Chem. Soc.*, 1922, **44**, 2212) and Tartar and Draves (*J. Physical Chem.*, 1926, **30**, 763) have shown that the negatively charged mastic sol is coagulated by different acids at approximately the same p_H, and that the coagulation concentration of salts is without significance unless the p_H of the sol is also specified. They have also shown that mastic sols are inherently acid solutions. It therefore appears that although platinum and mastic sols would seem to be markedly dissimilar in nature, yet they are in fact remarkably alike. Now platinum sols are definitely acid, and if their structure corresponds to that suggested by Pennycuick

(*loc. cit.*), they might be expected to show the same p_H on coagulation by different acids. This was found to be the case.

Acids of eight different types were used (see Table I), oxalic acid having to be discarded owing to its undergoing slight decomposition. All the work was carried out in borosilicate vessels, and conductivity water ($\kappa < 1$ gemmho) was used for dilutions. The method of coagulation was that adopted in Part I of this series (*loc. cit.*). The approximate coagulation concentration was first obtained by preliminary tests, and then the acid solutions were made of such concentrations as to have comparable powers of coagulation, so that at coagulation the platinum sol would always suffer the same dilution. The coagulation was determined after standing for 24 hours. The p_H values of the clear supernatant liquids were measured by the quinhydrone electrode at 30°, after the platinum had settled out. Determinations were always carried out in pairs, and if one pair showed a variation greater than 0·01 unit a second pair was taken. In Table I, the concentrations required for

TABLE I.

Hydrogen-ion concentration of platinum sol = 3×10^{-5}.

Acid.	Coag. *conc.*	p_H.	[H+] at *coag.*	[H+] of *acid alone.*	*Difference.*
Hydrochloric	0·196	3·69	20×10^{-5}	18×10^{-5}	2×10^{-5}
Sulphuric	0·184	3·69	20 ,,	17 ,,	3 ,,
Nitric	0·192	3·66	22 ,,	18 ,,	4 ,,
Benzoic	0·820	3·63	23 ,,	21 ,,	2 ,,
Tartaric	0·500	3·59	25 ,,	20 ,,	5 ,,
Salicylic	0·295	3·57	26 ,,	24 ,,	2 ,,
Succinic	2·135	3·57	26 ,,	24 ,,	2 ,,
Citric	1·200	3·44	36 ,,	31 ,,	5 ,,

coagulation (col. 2) are given in milliequivs. of titratable hydrogen per litre, calculated on the total volume of platinum and added acid. (The maximum error in the hydrogen-ion concentrations in cols. 4 and 5 is 1×10^{-5}, and therefore that in col. 6 is 2×10^{-5}.)

The coagulation occurs within a narrow p_H range, *viz.*, 3·44—3·69. It can therefore be concluded that the hydrogen-ion concentration is the controlling factor in the coagulation of colloidal platinum by acids. The variation in the p_H at coagulation, although small, is nevertheless real. Part at least of this is due to a decided difference in the rates at which the coagulating particles coalesce and become visible. Although readings were taken only after the solutions had stood for 24 hours, it was observed that with the acids towards the top of the table no further changes took place after about 8 hours, but with the acids towards the bottom of the table the actual flocculation appeared to be a much slower process. It is evident,

however, that the part played by the anion is often negligible and always very small.

The values of the hydrogen-ion concentrations (col. 4), when compared with the normalities of the coagulating acids (col. 2), appear to be too high, for the three mineral acids give hydrogen-ion concentrations which indicate slightly more than 100% ionisation. The platinum sols, however, were originally acid, and it would therefore appear that some (at least) of this acidity still remains even after the platinum is all precipitated. To test this point, solutions of the various acids were prepared of concentrations exactly equal to the coagulatory concentrations shown in col. 2, and their hydrogen-ion concentrations were then determined as before; the results, given in col. 5, show that the supernatant liquor after the platinum has been coagulated is more acid than a pure acid solution of exactly the same concentration of added acid, the excess acidity being given in the last column. The platinum sol used for these coagulations had an initial hydrogen-ion concentration of 3×10^{-5} and $\kappa_{30^\circ} = 18$ gemmhos. From cols. 4 and 5 it appears that the *total acidity after coagulation is approximately the initial natural acidity plus the acidity of the added acid, i.e., during the coagulation process no acid is removed.*

Conductimetric Investigation.—As was shown in Part II (*loc. cit.*), the weak solutions involved respond to conductimetric investigation with a remarkable degree of accuracy, and such methods were therefore expected to give more exact information concerning the non-removal of acid during the coagulation process. Briefly, the method adopted consisted in placing a good conductivity water ($\kappa = 0{\cdot}6$ gemmho) in the cell, adding increasing quantities of acid, and plotting the specific conductivity–acid concentration curve. The same quantity of platinum sol was then placed in the cell, and the experiment repeated. A comparison of the resulting curves gave the necessary information.

Three cells, of the type previously described, were used (constants 0·0109, 0·0204, and 0·0212). They were washed with conductivity water and air-dried before use. The acids were added from 3 c.c.-burettes, and during the whole process the cells were strictly air-tight. After each addition, the solutions were stirred by a carbon dioxide-free air stream passing through a wash-bottle in the bath. The temperature of the experiment was 30°. Four acids were used, *viz.*, hydrochloric, nitric, tartaric, and citric, as being representative of those given in Table I. The concentration and quantity of the added acid were previously calculated, so that in the case of the platinum sols the whole of the platinnm would not only be coagulated but completely deposited, leaving the solution quite

clear. As would be expected from the foregoing work, hydrochloric and nitric acids caused coagulation at approximately the same specific conductivity, *viz.*, 190 gemmhos for the particular sol used, tartaric acid at a slightly higher conductivity, 200 gemmhos, and citric at a still higher conductivity, 280 gemmhos. Hydrochloric and nitric acids showed strictly comparable curves under all conditions, and accordingly results for the former only are detailed. The behaviour of the two organic acids showed no outstanding differences, and only the results for tartaric acid are quoted. The results are set out in Tables II and III, and the corresponding curves in Figs. 1

TABLE II.

Normality of added HCl, 0·004*N*. Volume of solution initially in cell, 37 c.c. Pt sol boiled for 50 minutes, $\kappa = 22{\cdot}3$.

(A). Water of $\kappa = 0{\cdot}61$.		(B). Pt sol of $\kappa = 22{\cdot}3$.		(C). HNO_3 of $\kappa = 21{\cdot}5$.		(D). Tartaric acid of $\kappa = 22{\cdot}3$.	
(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).
—	0·61	—	22·3	—	21·5	—	22·3
28	12·86	27·8	33·9	26·9	33·28	33	34·08
60	26·45	60	47·67	58·6	47·28	76	50·98
91	40·28	91	61·44	89·9	61·30	119	68·15
121	53·47	122	74·64	121	74·74	158	84·85
157	69·97	156	89·74	155	90·46	198	101·5
201	89·1	203	109·6	199	110·1	237	117·9
230	102·4	232	122·0	229	123·1	273	133·8
270	120·8	276	141·8	277	144·4	312	149·8
325	144·3	323	162·5	324	164·9	348	165·7
391	174·2	388	190·5	369	185·0	383	180·4
434	193·6	433	210·4	413	204·8	418	196·5
468	207·4	468	226·1	456	223·9	452	211·0
531	236·5	557	264·5	538	260·1	517	239·2

TABLE III.

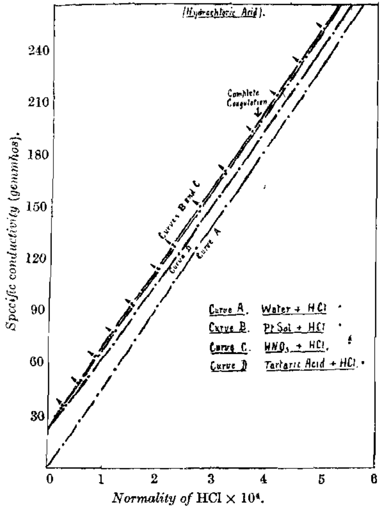
Normality of tartaric acid added, 0·01*N*. Volume of solution initially in cell, 37 c.c. Pt sol boiled for 50 minutes, $\kappa = 23{\cdot}1$.

(A). Water of $\kappa = 0{\cdot}54$.		(B). Pt sol of $\kappa = 23{\cdot}1$.		(C). HNO_3 of $\kappa = 22{\cdot}9$.		(D). Citric acid of $\kappa = 23{\cdot}6$.	
(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).	(*a*).	(*b*).
—	0·54	—	23·1	—	22·9	—	23·64
67	19·7	67	40·5	83	43·51	67·1	38·19
152	38·0	146	57·5	196	66·0	149	54·16
230	53·5	225	72·4	298	84·96	225	67·63
304	67·17	299	85·4	404	102·1	297	79·91
390	82·40	382	99·3	502	117·1	384	93·63
498	99·3	491	116·2	600	131·1	494	109·7
569	110·1	571	126·9	695	144·1	567	119·9
671	125·2	678	141·2	796	156·6	673	134·2
789	140·2	789	156·2	896	168·6	791	150·2
884	152·2	882	167·7	991	180·5	882	160·8
847	160·4	971	178·6	1080	191·2	947	168·6
1054	173·7	1076	190·9	1169	201·1	1059	181·5
1136	183·7	1161	200·7	1260	210·8	1165	192·3
1290	201·1			1340	219·8	1254	203·2

and 2. In each table column (*a*) gives 10^6 times the concentration of added hydrochloric acid (Table II) or tartaric acid (Table III) based on the total volume of the resulting solution, and column (*b*) gives the specific conductivity (κ) in gemmhos.

In Figs. 1 and 2, curves A represent the specific conductivities of the pure acid at various concentrations, whilst curves B represent the specific conductivities of the platinum sol at corresponding

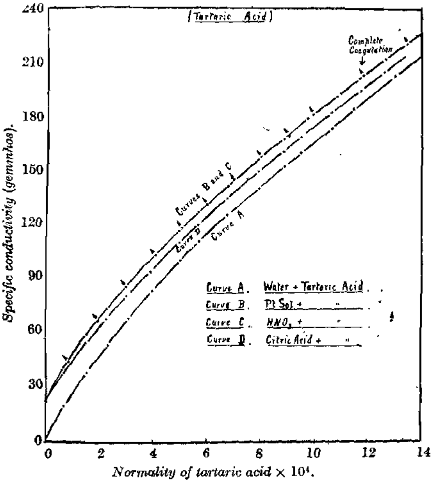
FIG. 1.



(added) acid concentrations. The latter curves go well past the coagulation points. It is at once evident that after coagulation the total conductivity of the solution is the approximate sum of the initial and added acid conductivities, thus confirming the conclusion from the foregoing determinations of p_H, that *during the coagulation process no acid is removed*. It might be objected, however, that the slight convergence of the curves indicates an actual removal of the acid. This is not so, for it will be noticed that the convergence of the curves still persists *even after all the platinum has been precipitated*.

(This was also the case with the curves which have been omitted.) It must therefore be concluded that during coagulation none of the initial nor of the added acid is removed. The convergence of the A and B curves is due to either or both of the following: (*a*) the mutual repression of ionisation of the platinum acid and the added acid, (*b*) the diluting effect of the added acid on the volume of the platinum sol taken and therefore on the platinum acid present. The latter effect is inherent in the method used and can be calculated

FIG. 2.



from the dilution figures. Since 37 c.c., the original volume of the platinum sol, always received a total addition of 5 c.c. of acid, the conductivity due to the platinum acid should be decreased in the ratio 42 : 37. This decrease coincides so closely with the experimental convergence of the curves, particularly when they are plotted on a larger scale, that the first explanation can be ruled out, and it is concluded that the added acid does not materially repress the ionisation of the natural platinum acid, which therefore behaves as a strong acid. This conclusion was completely confirmed by

replacing the platinum sol with a strong acid of the same conductivity and repeating the experiment.

To this end some conductivity water was placed in the cell, and nitric acid added in very small amounts until the solution showed a specific conductivity approximately that of the platinum sol used. Conditions were so arranged that the total volume was now 37 c.c. The solution then received increments of hydrochloric acid under exactly the same conditions as the platinum sol. The results are set out in column C of Table II and curve C in Fig. 1. Curves B and C are extremely close together, but in view of the fact that the experimental error is so small as to be represented by the size of the dots in the figure, it would appear that the platinum-sol curve, B, *actually falls very slightly below the strong-acid curve*, C.

If, on the other hand, a dilute solution of tartaric acid ($\kappa = 22{\cdot}3$ gemmhos) is treated in exactly the same way, the resulting curve (D, Fig. 1; see col. D, Table II) falls well below the corresponding B and C curves. This is what would be expected and is due to the depression of the ionisation of the weak tartaric acid by the strong hydrochloric acid.

On repeating these experiments, starting with dilute solutions of nitric and of citric acid, and adding tartaric acid, corresponding results were obtained (see columns C and D, Table III; curves C and D, Fig. 2). In this case, however, there is no measurable difference between the platinum-sol curve (B) and the strong-acid curve (C). Strictly comparable results were obtained when citric acid was the added acid.

From these results two conclusions stand out: first, that during coagulation no acid is removed, and secondly, that the natural acid originally present in the platinum sol is a strong acid comparable in strength with nitric acid.

An attempt was made to follow the p_H–acid concentration changes for the above solutions. As with the previous p_H measurements the technique proved difficult and the experimental error was high. One set of results only is quoted (Table IV); it shows the hydrogen-ion concentrations of a range of hydrochloric acid solutions and those of platinum solutions of the same (added) hydrochloric acid concentration.

TABLE IV.

Pt sol of $[H^+] = 4 \times 10^{-5}$.

$[H^+]$ of acid alone, $\times 10^5$	13	24	34	44
$[H^+]$ of Pt sol, $\times 10^5$	16	26	37	47
Difference $\times 10^5$	3	2	3	3

These, and in fact all the results obtained by this method, show

definitely that after coagulation the solution has a higher acidity than that due to the added acid, but so far the *E.M.F.* results afford only qualitative support to the above conductimetric work. This evidence is of value, however, for it shows by the most direct method that in platinum sols we are undoubtedly dealing with acid solutions.

Discussion.

In Part II (*loc. cit.*) it was suggested that the colloidal platinum particles consisted of aggregates containing both atoms of platinum and complex anions of probable constitution PtO_4. The anions formed a protecting ionised surface to the colloidal particles. It was further suggested that the positive kations, the hydrogen ions, were free, and as such could be titrated with bases. The present work, while supporting the general nature of this structure, reveals some essential differences. Although the platinum particles are of the structure outlined, the results now indicate that their hydrogen-ion partners are not free but form a double layer at the surface. The free strong acid in solution would appear to be a platinic acid, and although no valid alternative interpretation of these results is available, yet it is surprising that such an acid should be capable of existence in the free state, and still more so that it should behave as a strong acid. The presence of this acid accounts for the stability of the sols and for their ease of preparation in the purest conductivity water. Further, the acidity and the conductivity of platinum sols is due entirely to this free acid, and it remains in solution after all the platinum has been coagulated.

The increase in acidity (and conductivity) on boiling or on ageing is tentatively accounted for as follows: The colloidal platinum particles consist of atoms of platinum plus PtO_4 anions. At high temperatures some of these, probably the larger, suffer disintegration. This disintegration sets free a certain number of PtO_4 anions which with their hydrogen-ion partners form platinic acid. Part of the disintegrated particle thereby becomes unstable and forms a slight precipitate such as is always produced on boiling. Ultra-microscopic investigations are now being carried out which will probably throw further light on the coagulation process.

The similarity in nature between solutions of colloidal platinum and of mastic is now emphasised. Tartar and Draves's mastic sols (*loc. cit.*) were definitely acid (p_H 4·08—3·47), and by ultra-filtration and dialysis the acidity was traced to organic acids in true solution. Moreover, after coagulation the solutions retained their original acidity. Rabinowitsch and Burstein (*Biochem. Z.*, 1927, **182**, 110) titrated mastic sols with alkali and obtained conductivity

curves with sharp minima, and Hotta (*ibid.*, **183**, 72) confirmed the acid nature of the sols by electrometric measurements. They also found that both the conductivity and the hydrogen-ion concentration increased on keeping.

Summary.

The previous work revealing the acid nature of colloidal platinum sols is confirmed by direct measurement of the p_H with the quinhydrone electrode. Such measurements show that platinum sols become more acid on keeping or on boiling.

It is shown that the coagulation of colloidal platinum by acids occurs at an almost constant p_H.

Definite evidence is produced that during the coagulation by acids no acid is removed by the platinum particles.

It is shown that the natural acidity of platinum sols is due to a free acid, probably platinic acid, which at these low concentrations behaves as a strong acid.

Note added, January 14th, 1928.—Further work indicates that the acid is hexahydroxyplatinic acid, $H_2Pt(OH)_6$. S. W. P.

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SOUTH AUSTRALIA. [*Received, January 16th, 1928.*]

LXXII.—*The Budde Effect with a Mixture of Bromine Vapour and Air.*

By ERNEST BROWN and DAVID LEONARD CHAPMAN.

BUDDE (*Pogg. Ann.*, 1871, **144**, 213) observed that chlorine expands on exposure to light, and suggested that the effect might be due to the dissociation of chlorine molecules into atoms; but later [*Pogg. Ann.* (*Ergb.*), 1873, **6**, 477], he showed that the expansion was accompanied by a rise in temperature, which was of sufficient magnitude to account for the increase in volume.

Several investigators have asserted that dry chlorine does not exhibit the Budde effect; but none, with the exception of Shenstone (J., 1897, **71**, 471), describes experiments in support of the assertion. Moreover, as the single experiment reported by Shenstone is unconvincing, there is not at present, in our opinion, sufficient reason for accepting the view that dry chlorine does not exhibit the Budde effect.

Recently, however, both Ludlam (*Proc. Roy. Soc. Edin.*, 1924 **44**, 197) and Lewis and Rideal (J., 1926, 583) have described

experiments which appear to demonstrate conclusively that a dry mixture of pure bromine vapour and air does not expand when exposed to light. Their published data show that the effect of desiccation becomes appreciable when the degree of dryness reaches that attainable by leaving a gas in contact with concentrated sulphuric acid, and that after thorough drying with phosphorus pentoxide no Budde effect at all can be detected.

Using rather different methods of experiment from those adopted by Ludlam and by Lewis and Rideal, and taking what appear to us to be reasonable precautions, we have obtained results which seem to indicate that the Budde effect with a mixture of air and bromine is not diminished to any measurable extent by drying.

Experimental.

The bromine was bought as pure, and was subjected to the process of purification recommended by Scott (J., 1913, **103**, 847). The last traces of chlorine (if any) were then removed by distilling it from a solution of potassium bromide (previously freed from iodine), and the last traces of hydrobromic acid by shaking it with a very dilute solution of potash, separating, and finally distilling it from moist zinc oxide.

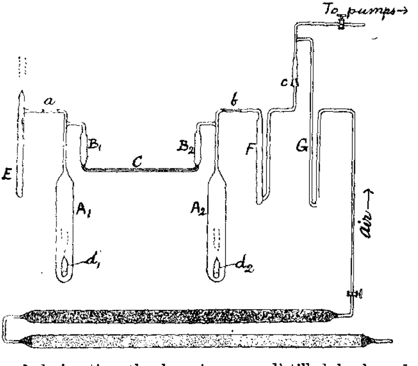
The phosphorus pentoxide was distilled in a current of oxygen, as described by Finch and Fraser (J., 1926, 117). The product was very pure, and the yield good. It melted to a perfectly clear liquid, did not reduce either silver nitrate or mercuric chloride, and contained a large proportion of the volatile form.

The apparatus is depicted in Fig. 1. The section to the left of the ground glass joint, *c*, was constructed of Pyrex glass. This was cleaned with chromic acid solution, washed with hot distilled water, and quickly dried. Whilst the glass was still warm, phosphorus pentoxide was introduced into the tube *E*, and into the tubes A_1 and A_2 through the tubulures d_1 and d_2. About 4 c.c. of bromine, which had been kept for some days in contact with phosphorus pentoxide, were introduced into *E*. *E*, d_1, and d_2 were then sealed by the blowpipe. The apparatus was next brought into connexion with the pumps by means of the ground glass joint, *c*, and the tube *E* and the U-tubes *F* and *G* were immediately afterwards surrounded with liquid air. The apparatus was then exhausted with a mercury-vapour pump backed by a Sprengel pump. After a high vacuum had been obtained, the lower portion of the tubes A_1 and A_2, to slightly above the level of the phosphorus pentoxide, were surrounded with water contained in shallow basins, and the rest of the apparatus, except the portions in the vacuum flasks, was strongly heated with the blowpipe while the pumps were in action. About 1 c.c. of the

bromine in E was then distilled into F. Air, which had already been freed from carbon dioxide and dried by phosphorus pentoxide, was then slowly admitted to the apparatus through the U-tube G. Most of the bromine contained in E was then distilled into A_1, and the portion of the apparatus between the short capillary tubes a and b was detached by sealing before the blowpipe.

Bromine "wets" phosphorus pentoxide and is rapidly drawn into the spaces between the crystals, and as the phosphorus pentoxide introduced into each of the tubes E, A_1, and A_2, was more than sufficient to absorb the whole of the bromine used, the drying of the liquid bromine must have been very rapid. To hasten the

FIG. 1.



process of desiccation the bromine was distilled backwards an forwards between the tubes A_1 and A_2 and the small bulbs B_1 an B_2, the distillation being effected by alternately cooling and warmir B_1 and B_2 and the connecting capillary tube, C. The phosphor pentoxide was not heated. The internal diameter of the tubes A and A_2 was 3 cm., and that of the capillary tube, C, 1 mm.

For the purpose of comparison, a similar apparatus was co structed of the same Pyrex tubing and filled with 4 c.c. of mo bromine and air at atmospheric pressure.

With this apparatus the measurement of the Budde eff presented no difficulty. A_1 and B_1 were surrounded with alumini foil which was painted black on the outside. A scale was attach to the capillary tube, C, which contained a thread of bromine ab

1 cm. long. On exposure of A_2 to light, the thread of bromine moved rapidly towards A_1, and it returned to its former position on the light being shut off. All the measurements recorded below were made *with the apparatus enclosed in a darkened thermostat* filled with water at 26°, the light being admitted to the thermostat through an oblong window of such a size that about one-half of the central portion of the insolation vessel was illuminated. The source of light was a 1000-watt, gas-filled, tungsten-filament lamp, placed with its filament at a distance of 30 cm. from the centre of the insolation vessel. In making the measurements, the white light was filtered either through a 25% solution of ferrous ammonium sulphate or through a 5% solution of sodium dichromate contained in glass troughs with parallel plane faces, and of the same dimensions.

A typical result is recorded below:

Light filtered through ferrous ammonium sulphate solution.

Time of drying (days)	Wet	79	396
Expansion (scale divisions)	57	50·6	53·5

The ratios of the expansion caused by exposure to light which had been filtered through the solution of sodium dichromate to that occasioned by exposure to light transmitted through the solution of ferrous ammonium sulphate, after different periods of drying, is given in the following table.

Time of drying (days)	Wet	22	61	72	126	396
Ratio of expansions ...	0·40	0·39	0·44	0·41	0·38	0·35

Conclusion.

The almost complete removal of water vapour alone from a mixture of bromine vapour and air does not prevent the mixture from exhibiting the Budde effect.

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JESUS COLLEGE, OXFORD. [*Received, December 29th*, 1927.]

LXXIII.—*The Nitration of Benzylaniline.*

By JOSEPH REILLY, JOHN J. MOORE, and PETER J. DRUMM.

MATZUDAIRA (*Ber.*, 1887, **20**, 1613), by nitrating dibenzylaniline in acetic acid solution, obtained 4-nitrophenyldibenzylamine, $NO_2{\cdot}C_6H_4{\cdot}N(CH_2Ph)_2$. Under such conditions we have found that benzylaniline does not nitrate in either ring, the nitrate of the base only being formed. On nitration with nitric and sulphuric acids, however, benzylaniline yields phenyl-3-nitrobenzylamine, $C_6H_5{\cdot}NH{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, and a small quantity of phenyl-4-nitrobenzylamine. Further work on this interesting result—unexpected

in view of recent theories on substitution, which indicate that nitration should occur in the *o*- and *p*-positions of the aniline ring —will be undertaken as soon as possible.

EXPERIMENTAL.

Nitric acid (*d* 1·5; 6·7 g.) was added to benzylaniline (18·3 g.) in acetic acid (500 c.c.); crystals of benzylaniline nitrate, m. p. 142° (decomp.), slowly separated (Found: N, 11·8. Calc. for $C_{13}H_{13}N,HNO_3$: N, 11·4%).

To a well-cooled solution of benzylaniline (10 g.) in concentrated sulphuric acid (150 c.c.) was added, with stirring, a solution of nitric acid (*d* 1·5; 3·7 g.) in concentrated sulphuric acid (20 c.c.), the temperature being maintained at about – 3°. The mixture was stirred for an hour at 0° and poured on crushed ice. The clear solution, when made alkaline in the cold with sodium carbonate solution, gave a reddish-orange precipitate (10 g.) which, crystallised from alcohol and finally from light petroleum (b. p. 60—80°), formed deep orange needles (6·5 g.), m. p. 84·5—85° (Found: N, 12·3. Calc. for $C_{13}H_{12}O_2N_2$: N, 12·3%). The residue obtained by evaporation of the alcoholic mother-liquor, on repeated crystallisation from light petroleum (b. p. 60—80°), gave yellow plates (1 g.), m. p. 70—72°, which were identified as phenyl-4-nitrobenzylamine by the melting point of a mixture with an authentic specimen.

The identity of the above substance (m. p. 84·5—85°) with phenyl-3-nitrobenzylamine was established by the mixed melting-point method and by comparison of their acetyl and benzoyl derivatives.

Acetophenyl-3-nitrobenzylamide was prepared by Purgotti and Monti (*Gazzetta*, 1900, **30**, 257) by heating phenyl-3-nitrobenzylamine with acetic anhydride in a sealed tube at 130° for 3 hours, and obtained as yellow needles, m. p. 48°. It is more conveniently obtained by heating the nitroamine and acetic anhydride at the ordinary pressure in presence of anhydrous sodium acetate. It crystallised from benzene–light petroleum (b. p. 60—80°) in colourless plates (Found: N, 10·4. Calc. for $C_{15}H_{14}O_3N_2$: N, 10·4%), which melted, alone or when mixed with the acetyl derivative of the main product of nitration of benzylaniline, at 66—67°.

Benzophenyl-3-nitrobenzylamide, prepared in the usual manner crystallised from benzene–light petroleum (b. p. 60—80°) in colour less prisms (Found: N, 8·6. $C_{20}H_{16}O_3N_2$ requires N, 8·4%) Specimens prepared from phenyl-3-nitrobenzylamine and from th main product of nitration of benzylaniline melted, alone or whe mixed, at 103°.

UNIVERSITY COLLEGE, CORK. [*Received, December 29th, 1927.*]

LXXIV.—*Trimethylplatinum Acetylacetone, a Volatile Platinum Compound.*

By Robert Charles Menzies.

The separation of thallous iodide from solutions of thallous acetylacetone in ethyl or methyl iodide and the preparation of ethyl ethylacetoacetate by boiling a solution of ethyl thalloacetoacetate in ethyl iodide are particular instances of double decomposition between thallous salts and halides. The reaction is a general one for the preparation of acetylacetone derivatives, *e.g.*, ferric acetylacetone is obtained in 60% yield by heating one equivalent of ferric chloride with three equivalents of thallous acetylacetone. A new application of the method is the preparation, by reaction between thallous acetylacetone and trimethylplatinic iodide (Pope and Peachey, J., 1909, **95**, 571) in dry benzene, of *trimethylplatinum acetylacetone*, $Me_3Pt\genfrac{}{}{0pt}{}{\diagup O\cdot CMe}{\nwarrow O{:}CMe}\!\!\gg\! CH$, which is now described on account of its behaviour on heating.

Experimental.

Ferric acetylacetone (2·14 g.; yield, 61%) was obtained by refluxing 1·62 g. of anhydrous ferric chloride and 9·1 g. of thallous acetylacetone in dry ether. The reaction was completed in less than ½ hour and 6·3 g. of thallous chloride (yield, 88%) were also obtained. The first two crops (1·1 g. and 0·55 g.) had m. p. 185° and 182°, respectively (Hantzsch and Desch, *Annalen*, 1902, **323**, 13, found m. p. 179°; Urbain and Debierne, *Compt. rend.*, 1899, **129**, 303, found m. p. 184°).

Trimethylplatinic iodide (7·5 g.) was prepared from chloroplatinic acid (20 g.) by Pope and Peachey's method (*loc. cit.*). Great difficulty, however, was experienced in dissolving anhydrous platinic chloride in dry ether. It was therefore dissolved in the minimum quantity of absolute alcohol; this solution, on addition of ether, separated into two layers. The presence of the alcohol necessitated the use of a large excess of the Grignard reagent.

Trimethylplatinum Acetylacetone.—Solutions of 3·7 g. of trimethylplatinic iodide and 3·03 g. of thallous acetylacetone in warm benzene free from thiophen were mixed and heated under reflux, the thallous iodide that separated was removed, the filtrate evaporated to dryness, and the residue crystallised from hexane (charcoal). Two crops (1·6 g. and 0·8 g.) of *trimethylplatinum acetylacetone* were obtained

(yield, 70%) (Found: Pt, 57·0; C, 28·5; H, 4·9. $C_8H_{16}O_2Pt$ requires Pt, 57·5; C, 28·3; H, 4·75%).

This compound separates from hot benzene, on cooling, in colourless needles, but as thick plates on slow evaporation of a cold benzene solution. It is very soluble in the usual organic solvents and is most conveniently recrystallised from light petroleum or hexane. In 3% benzene solution it is associated (Found: *M*, cryoscopic, 576. Calc.: *M*, 339·2). A solution in methyl alcohol remains transparent on mixing with cold water, but on being heated the mixture becomes cloudy.

When heated in a capillary tube, trimethylplatinum acetylacetone decomposes at about 200° without melting; but in a dry tube or flask it sublimes, a little being deposited apparently unchanged on the cooler parts of the vessel. The vapour, however, is decomposed by hot glass, on which the platinum is deposited in a coherent form; by carefully heating and shaking a small quantity in a glass vessel, it is possible to coat much of the surface with a platinum mirror. Mirrors prepared in air at the ordinary pressure do not adhere firmly, being partly stripped, but not dissolved, by boiling nitric or hydrochloric acid. If, however, the glass be heated to a dull red heat after deposition, the metal adheres more firmly. When the compound was heated in the vacuum produced by a good water-pump, in a test-tube immersed in a sulphuric acid bath, sublimation began at 160°, the compound condensing above the level of the acid. Decomposition on the hot glass below the acid took place slowly at 160° and became rapid at 190°. Subsequent heating of the evacuated tube over a flame, and finally at a red heat after the platinum had been deposited, gave the most adherent mirror yet obtained; it was not stripped by boiling with water or nitric or hydrochloric acid.

THE UNIVERSITY, BRISTOL. [*Received, February 13th*, 1928.]

LXXV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part III.*

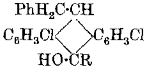
By EDWARD DE BARRY BARNETT and JAMES WILFRED COOK.

A. THE action of Grignard solutions upon anthrones has been further studied (for references to previous work, see Part II, J., 1927, 1724) with the following results.

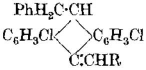
1. The dihydroanthranols (I) obtained from 1 : 5-dichloro-9-benzylanthrone could not be made to crystallise with the exception of the phenyl and benzyl compounds (I, R = Ph and CH_2Ph).

2. The methyl and benzyl compounds (I, R = Me and CH_2Ph,

respectively), on being heated with acetic acid containing a little hydrochloric or sulphuric acid, gave colourless and non-fluorescent methylene derivatives (II, R = H and Ph, respectively), but the phenyl compound, with which such a reaction is impossible, gave benzylphenyldichloroanthracene (III, R = Ph). From the remaining oily dihydroanthranols, only resinous products were formed, although from the *iso*propyl derivative *iso*propylbenzyldichloroanthracene (III, R = Pr^{β}) was obtained in very small yield. 1 : 5-Dichloro-9-benzylanthrone therefore resembles 1 : 5-dichloroanthrone (Barnett, Cook, and Matthews, *Ber.*, 1926, **59**, 2863), 1 : 5-dichloro-9-phenylanthrone (Barnett, Cook, and Wiltshire, J., 1927, 1724), and 1 : 5-dichloro-9-methylanthrone (Barnett and Cook, *Ber.*, 1928, **61**, 314) in its behaviour towards Grignard solutions.



(I.)



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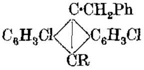
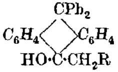


(III.)

3. Since the methylene derivative (II) might be formed either by direct loss of water or by the preliminary formation of an alkylanthracene and subsequent transannular migration of a hydrogen atom (Barnett and Cook, *loc. cit.*), dihydroanthranols (IV) were prepared by the action of magnesium methyl iodide and magnesium benzyl chloride on 9 : 9-diphenylanthrone, and the behaviour of these dihydroanthranols towards acetic acid containing a little mineral acid was studied. In both cases, transannular loss of water is impossible, but methylene derivatives (V) were readily formed.



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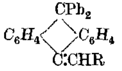

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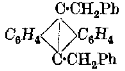
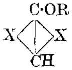


(VI.)

4. 9 : 9-Dibenzylanthrone gave well-crystallised dihydroanthranols on treatment with magnesium methyl iodide, magnesium phenyl bromide, and magnesium benzyl chloride. All of these became fluorescent on heating with acetic acid containing mineral acid. From the methyl and the phenyl compound no definite decomposition product could be isolated, but from tribenzyldihydroanthranol considerable quantities of 9 : 10-dibenzylanthracene (VI) were obtained, and although the yield is poor this is probably the best method at present known of preparing this hydrocarbon. The formation of dibenzylanthracene from tribenzyldihydroanthranol must be due to transannular loss of benzyl alcohol (the acetic acid

liquor smelt strongly of benzyl acetate), and the reaction, which is an interesting one, is being further investigated.

B. Previous work on the action of alkyl halides and caustic alkali on anthrones (Goldman, *Ber.*, 1888, **21**, 1178, 2505; Hallgarten, *ibid.*, 1888, **21**, 2508; K. H. Meyer and Schlösser, *Annalen*, 1920, **420**, 130; Barnett, Cook, and Matthews, J., 1923, **123**, 391, 2631; *Ber.*, 1928, **61**, 314) has shown that one or more of the following products may result: anthranyl alkyl ether (VII), alkylanthranyl alkyl ether (VIII), alkylanthrone (IX, R = H), dialkylanthrone (IX).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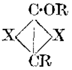

(VIII.)

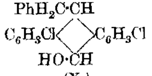
(IX.)

Which type of compound is produced in any given case depends both on the particular anthrone used and on the alkyl halide. The following further results have now been obtained:

1. 1 : 5-Dichloroanthrone when boiled with benzyl chloride and caustic potash gave an almost quantitative yield of benzyldichloroanthrone (IX, X = C_6H_3Cl, R = H, R′ = CH_2Ph). In this respect dichloroanthrone differs from anthrone itself, as the latter under similar conditions gives dibenzylanthrone (IX, X = C_6H_4, R and R′ = CH_2Ph) in about 40% yield, together with much resinous matter. This benzyldichloroanthrone can be neither methylated by means of methyl *p*-toluenesulphonate nor acetylated by boiling with acetic anhydride in pyridine solution. It can be reduced to the dihydroanthranol (X) by zinc dust and alcoholic ammonia.

2. 1-Chloro-9-anthrone (XI) (Barnett and Matthews, J., 1923, **123**, 2549; compare Eckert and Tomaschek, *Monatsh.*, 1918, **39**, 839) gave a dibenzyl compound which must be the dibenzylanthrone (IX) and not the benzylanthranyl benzyl ether (VIII), since it gives a dihydroanthranol (XIII) on treatment with magnesium phenyl bromide. The isomeric 1-chloro-10-anthrone (XII) (Barnett and Matthews, *loc. cit.*) gave only resinous products.

19.
1.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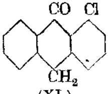
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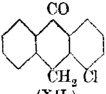
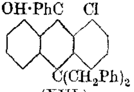
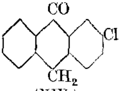
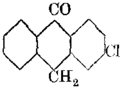

(XII.)

benzyl... ...hloro-9-anthrone (XIV) (future communication; compare of the ph... and Fischbach, *Ber.*, 1925, **58**, 1251) gave only resinous
2. The n...

products, easily soluble in ether, when boiled with benzyl chloride and caustic alkali, and presumably the isomeric 2-chloro-10-anthrone (XV) gives the same result, since no crystalline substance could be


(XIII.)


(XIV.)


(XV.)

isolated from the resinous product obtained by benzylating the crude mixture of isomerides prepared by reducing 2-chloroanthraquinone (Barnett and Matthews, *loc. cit.*).

4. Attempts to prepare unsymmetrical dialkylanthrones by benzylating 9-methylanthrone and 9-phenylanthrone yielded only resinous products.

5. 1 : 5-Dichloroanthrone and benzal chloride also gave only resinous substances.

It is possible that the failure to introduce more than one alkyl group into 1 : 5-dichloroanthrone is due to the hindering effect of one of the α-chlorine atoms, and this hindering effect may also account for the failure of 1 : 5-dichloroanthrone to give a benzylidene derivative with benzaldehyde in the presence of piperidine, and for the failure of 1 : 5-dichloroanthracene to give a ketone on treatment with benzoic anhydride and aluminium chloride (compare Cook, J., 1926, 1282, 2160). The data at present available, however, are insufficient to permit useful speculation on the causes influencing these reactions.

EXPERIMENTAL.

Action of Grignard Solutions on 1 : 5-*Dichloro*-9-*benzylanthrone*.—The finely powdered anthrone was slowly added to an ethereal solution of the Grignard reagent (3 mols.), cooled in a freezing mixture. After being kept in the freezing mixture for an hour and at the ordinary temperature for 4 hours, the whole was poured on a mixture of ice and solid ammonium chloride, and the washed ethereal solution evaporated to dryness on the water-bath. As a rule a viscous oil was left, but when magnesium benzyl chloride was used 1 : 5-*dichloro*-9 : 10-*dibenzyl*-9 : 10-*dihydroanthranol* (I, R = CH_2Ph) was obtained in the solid state; after recrystallisation from acetone, it formed snow-white needles, m. p. 197° (Found : Cl, 15·8. $C_{28}H_{22}OCl_2$ requires Cl, 15·7%).

The oil obtained when magnesium phenyl bromide was employed became solid on the addition of alcohol, and after recrystallisation from mixtures of acetone–aqueous alcohol and benzene–light petroleum 1 : 5-*dichloro*-10-*phenyl*-9-*benzyl*-9 : 10-*dihydroanthranol*-10

(I, R = Ph) *formed colourless, glistening crystals*, m. p. 167° (*Found: Cl*, 16·5. $C_{27}H_{20}OCl_2$ *requires Cl*, 16·5%).

The dehydration of the dihydroanthranols was effected by heating on the water-bath for 1—3 hours in glacial acetic acid solution to which a little hydrochloric or sulphuric acid had been added. The following compounds were obtained:

1 : 5-*Dichloro*-9-*benzyl*-10-*methylene*-9 : 10-*dihydroanthracene* (II, R = H). From the crude dihydroanthranol obtained by means of magnesium methyl iodide. Snow-white crystals, m. p. 123°, from alcohol (Found: Cl, 20·2. $C_{22}H_{16}Cl_2$ requires Cl, 20·2%).

1 : 5-*Dichloro*-9-*benzyl*-10-*benzylidene*-9 : 10-*dihydroanthracene* (II, R = Ph). From the crystalline dihydroanthranol described above. Snow-white crystals, m. p. 158°, from glacial acetic acid (Found: Cl, 16·5. $C_{28}H_{20}Cl_2$ requires Cl, 16·6%).

1 : 5-*Dichloro*-9-*benzyl*-10-iso*propylanthracene* (III, R = Pr^{β}). A glacial acetic acid solution of the crude dihydroanthranol obtained by the action of magnesium *iso*propyl bromide was kept over-night at the ordinary temperature after a little hydrochloric acid had been added. The yellow crystals which separated were freed from red resinous matter by recrystallisation from ethyl acetate–alcohol and finally from alcohol. The substance then formed yellow plates, m. p. 138°, and exhibited a green fluorescence when in solution (Found: C, 76·2; H, 5·4. $C_{24}H_{20}Cl_2$ requires C, 75·9; H, 5·3%).

1 : 5 - *Dichloro* - 10 - *phenyl* - 9 - *benzylanthracene* (III, R = Ph). Obtained in 90% yield from the crystalline dihydroanthranol by heating on the water-bath with glacial acetic acid containing hydrochloric acid. After recrystallisation from toluene, it formed glistening, yellow crystals which melted at 213° either alone or when mixed with an authentic sample (Barnett, Cook, and Wiltshire, J., 1927, 1732).

Action of Grignard Solutions on 9 : 9-*Diphenyl- and* 9 : 9-*Dibenzylanthrone*.—In each case the finely powdered anthrone was slowly added to the well-cooled Grignard solution (1½—2 mols.). After being kept for 10—30 minutes in the freezing mixture and for 3—4 hours at the ordinary temperature (or over-night in the ice chest), the whole was poured on a mixture of ice and solid ammonium chloride, and sufficient ether added to dissolve the dihydroanthranol. The washed and filtered ethereal solution was then evaporated to dryness on the water-bath. The following compounds were obtained:

9 : 9-*Diphenyl*-10-*methylene*-9 : 10-*dihydroanthracene* (V, R = H). The dihydroanthranol formed by the action of magnesium methyl iodide on diphenylanthrone could not be obtained pure owing to the ease with which loss of water took place. The crude product

was therefore heated on the water-bath for 30 minutes with 8 parts of glacial acetic acid containing a little hydrochloric or sulphuric acid; the solid which separated on cooling crystallised from ethyl acetate *in colourless prisms*, m. p. 192° (Found: C, 93·9; H, 5·9. $C_{27}H_{20}$ requires C, 94·2; H, 5·8%).

9 : 9-*Diphenyl*-10-*benzyl*-9 : 10-*dihydroanthranol*-10 (IV, R = Ph), recrystallised from mixtures of benzene–alcohol and benzene–light petroleum, formed colourless needles, m. p. 228—230° (Found: C, 90·2; H, 6·1. $C_{33}H_{26}O$ requires C, 90·4; H, 5·9%).

9 : 9-*Diphenyl*-10-*benzylidene*-9 : 10-*dihydroanthracene* (V, R = Ph). From the above dihydroanthranol by heating on the water-bath with acetic acid containing hydrochloric or sulphuric acid. Colourless, glistening crystals, m. p. 254—255°, from toluene (Found: C, 94·1; H, 5·8. $C_{33}H_{24}$ requires C, 94·3; H, 5·7%).

9 : 9-*Dibenzyl*-10-*methyl*-9 : 10-*dihydroanthranol*-10. Snow-white crystals, m. p. 175°, from aqueous acetone (Found: C, 88·8; H, 6·6. $C_{29}H_{26}O$ requires C, 89·2; H, 6·7%).

10-*Phenyl*-9 : 9-*dibenzyl*-9 : 10-*dihydroanthranol*-10. Snow-white crystals, m. p. 189°, from acetone; gave a positive iodoform test (Found: C, 87·1; H, 6·7. $C_{34}H_{28}O,C_3H_6O$ requires C, 87·1; H, 6·7%).

9 : 9 : 10-*Tribenzyl*-9 : 10-*dihydroanthranol*. Colourless, hygroscopic crystals, m. p. 140°, from benzene–light petroleum (Found: C, 90·1; H, 6·6. $C_{36}H_{30}O$ requires C, 89·8; H, 6·8%).

9 : 10-*Dibenzylanthracene* (VI). Tribenzyldihydroanthranol was dissolved in hot glacial acetic acid, a little concentrated hydrochloric acid added, and the whole heated for 4 hours on the water-bath. Colourless crystals separated from the hot solution and after cooling were collected and recrystallised from toluene. They then melted at 245° alone or mixed with an authentic sample of dibenzylanthracene prepared by a different method (future communication).

Action of Alkyl Halides and Caustic Alkali on Anthrones.—1 : 5-*Dichloro*-9-*benzylanthrone* (IX, X = C_6H_3Cl, R = H, R′ = CH_2Ph). Fifty g. of 1 : 5-dichloroanthrone and 100 c.c. of benzyl chloride were boiled under reflux with 75 g. of potassium hydroxide in 300 c.c. of water until the black tar at first formed had completely vanished (about 2 hours). After cooling, the pasty product was washed with water by decantation and then agitated with ether. The almost colourless crystals thus formed were snow-white after recrystallisation from toluene or from ethyl acetate and then melted at 169° (Found: Cl, 20·3. $C_{21}H_{14}OCl_2$ requires Cl, 20·1%).

This anthrone gives a red solution in alcoholic alkali, but cannot be methylated even by prolonged treatment with methyl *p*-toluenesulphonate and potassium hydroxide in alcoholic solution, and in

this way resembles 1 : 5-dichloro-9-phenylanthrone (Barnett and Matthews, *Ber.*, 1926, **59**, 670). On the other hand, whereas phenyldichloroanthrone is easily acetylated by pyridine and acetic anhydride (Barnett and Matthews, *loc. cit.*), benzyldichloroanthrone cannot be acetylated by this method, and was recovered unchanged even after boiling for 12 hours with acetic anhydride and picoline bases (b. p. 140—145°).

1 : 5-*Dichloro*-9-*benzyl*-9 : 10-*dihydroanthranol*-10 (X). Dichlorobenzylanthrone was recovered unchanged after boiling with hydriodic acid and red phosphorus in glacial acetic acid solution and was not reduced by zinc dust and aqueous ammonia. The reduction to the dihydroanthranol was effected by heating 5 g. with 15 g. of zinc dust and 150 c.c. of alcoholic ammonia (7·5% NH_3) on the water-bath for 4 hours. The crystals which separated from the filtrate on cooling became colourless on recrystallisation from alcohol and then melted at 179°. They contained no nitrogen (Found : C, 70·7 ; H, 4·7. $C_{21}H_{16}OCl_2$ requires C, 71·0 ; H, 4·5%). Facile trans-annular loss of water with formation of 1 : 5-dichloro-9-benzyl-anthracene (identified by direct comparison with an authentic sample) was brought about by heating on the water-bath with acetic acid containing a little hydrochloric acid.

1-*Chloro*-10 : 10-*dibenzylanthrone*. Five g. of 1-chloro-9-anthrone were boiled under reflux for 2 hours with 10 c.c. of benzyl chloride and 7 g. of potassium hydroxide in 30 c.c. of water. The cooled pasty product was washed with water and agitated with ether and the resulting almost colourless solid was recrystallised from glacial acetic acid. It was then snow-white, melted at 223°, and gave no colour with a boiling alcoholic solution of potassium hydroxide (Found : C, 82·1 ; H, 5·3. $C_{28}H_{21}OCl$ requires C, 82·2 ; H, 5·3%).

1-*Chloro*-9-*phenyl*-10 : 10-*dibenyl*-9 : 10-*dihydroanthranol*-9 (XIII). Five g. of the above dibenzylchloroanthrone were added to an ethereal solution of magnesium phenyl bromide prepared from 0·7 g. of magnesium. During the addition the solution was cooled in a freezing mixture, and after being kept for 5 hours at the ordinary temperature the whole was poured on a mixture of ice and solid ammonium chloride. The solid which separated was collected, and a small amount of rather less pure material was obtained by evaporating the ethereal layer of the filtrate. After recrystallisation from acetone it was snow-white and melted at 260° (Found : Cl, 17·1 $C_{34}H_{27}OCl$ requires Cl, 7·3%).

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JEWRY ST., E.C. 3. [*Received, December 31st, 1927.*]

LXXVI.—*A Contribution to the Stereochemistry of Tervalent Nitrogen.*

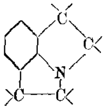
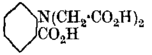
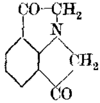
By JOSEPH GILBERT JACKSON and JAMES KENNER.

ALTHOUGH the Hantzsch–Werner hypothesis has been fully substantiated through the researches of Mills and his collaborators as a means of explaining the isomerism of the oximes and similar compounds, its application to compounds in which three separate groups are attached to the nitrogen atom has been much less successful. It is unnecessary to refer in detail to the earlier work, since this has been critically reviewed by Meisenheimer (*Ber.*, 1923, **56**, 1353; 1924, **57**, 1715, 1744; *Annalen*, 1924, **438**, 217), to whom we owe valuable contributions to the subject. At the present time, the evidence in favour of a non-planar configuration of compounds of tervalent nitrogen is to be seen in the dipolarity of the ammonia molecule, which confers on it the capacity of participation in metal-ammine formation (compare Magnus, *Z. anorg. Chem.*, 1922, **124**, 289; Hund, *Z. Physik*, 1925, **31**, 82); the existence of quinuclidine (compare Meisenheimer, *Annalen*, 1920, **420**, 190); a difference in the readiness with which the two forms of 4 : 5-dimethoxy-4 : 5-dihydroglyoxalone are converted into 5-methoxy-4 : 5-diphenyl*iso*glyoxalone (Biltz, *Annalen*, 1909, **368**, 156; *Naturwiss.*, 1926, **29**, 1678); the work of Moore (P., 1914, **30**, 183); and the isomerism of methyl*iso*pelletierine with *dl*-methylconhydrinone (Hess, *Ber.*, 1919, **52**, 1622; 1920, **53**, 129; Hess and Grace, *Annalen*, 1925, **441**, 101). But, apart from this last instance, the search for isomerides demanded by a non-planar configuration has been unsuccessful, and it would therefore appear that in general the non-planar readily passes into a planar form, from which the original or its enantiomorph may be regenerated, or else that the normal configuration is plane (compare Meisenheimer, *Ber.*, 1924, **57**, 1747).

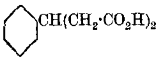
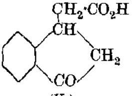
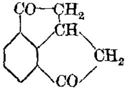
Before, however, such conclusions can be accepted, it is desirable that the negative results on which they rest should be supplemented by positive evidence. This would be supplied by the preparation of a compound in the molecule of which a nitrogen atom is common to two ring-structures, which are at the same time plane and coplanar. Since, so far as we know, there is no evidence available which renders doubtful the plane configuration of five-membered ring structures, it would appear that these conditions would be fulfilled by a structure of type (I), if Kekulé's formula for benzene and its derivatives be accepted.

The validity of the latter provision, however, requires examination, since the evidence of crystal structure indicates the possibility that the

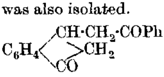
benzene nucleus may not always be plane. It was therefore desirable, before proceeding to work in the direction indicated on nitrogen compounds, to examine the behaviour of a compound, otherwise analogous, but containing in place of the nitrogen atom that of an element of which the stereochemical relationships are known to be closely similar to those postulated for nitrogen by the Hantzsch–Werner hypothesis. Since, then, anthranilodiacetic acid (II) appeared from the literature to be readily accessible, and the conditions suitable for the formation of the indoxylic ring structure, on which (III) is based, are well known, β-phenylglutaric acid (IV) was selected as its analogue for preliminary work.

(I.)   (II.)  (III.)

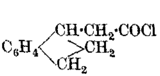
β-Phenylglutaric acid was easily converted under the influence of sulphuric acid into 1-*ketohydrindene*-3-*acetic acid* (V), but a careful search for any non-acidic, ketonic product, such as (VI), was unsuccessful. Similarly β-*phenylglutaryl chloride* underwent only

 (IV.)  (V.)  (VI.)

partial internal condensation under the influence of aluminium chloride. In the first experiments on this reaction, the light petroleum used as solvent was not purified, so that a ketonic product corresponding in composition to *ω*-3-*hydrindonylacetophenone* (VII) was also isolated.

 (VII.)

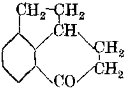
$C_6H_5·CH(CH_2·COPh)_2$ (VIII.)

 (IX.)

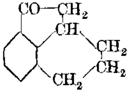
Its nature was demonstrated by its absence from among the products of reaction when aromatic components were removed from the solvent, and by its reappearance when benzene was added to the mixture employed. The formation of (VII) rather than αγε-triphenylpentane-αε-dione (VIII) under these conditions is an interesting illustration of the usual tendency towards intra- rather than inter-molecular condensation, and throws into stronger relief the significance of the failure to obtain (VI).

These results accord with the earlier observation by von Braun, Danziger, and Kohler that α-hydrindylacetyl chloride (IX) cannot be made to undergo internal condensation and, it may be noted, the combined results supply direct evidence against Sachse's benzene formula, according to which the ring system of (VI) is almost free from strain.

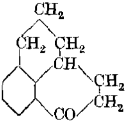
On the other hand, the results are in accord with the Kekulé formula and support, although possibly they do not finally demonstrate, the truth of the suggestion that two five-membered rings associated with a benzene nucleus in the manner contemplated must be coplanar. In regard to these rings, it was recognised that, for the present purpose, current views in regard to the configuration of saturated ring structures make it necessary to limit the number of atoms composing the ring to five. Experimental confirmation of this has recently been supplied by von Braun and Reutter, who were able to prepare the ketones (X), (XI), and (XII) by the Friedel–Crafts reaction (*Ber.*, 1926, **59**, 1922).*



(X.)



(XI.)



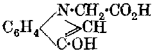
(XII.)

The fact that these compounds can be prepared serves at least to weaken any objection to the test here proposed, based on a possible difference in readiness of condensation between the 1 : 2- and the 1 : 6-positions in the benzene nucleus when the two are to be operative simultaneously (compare Marckwald, *Ber.*, 1890, **23**, 1015; *Annalen*, 1893, **274**, 331; 1894, **279**, 1).

A more serious defect lies in the fact that a valency angle of 120° in the case of a nitrogen atom might be sufficiently great to inhibit the possibility of forming the ring system (III). Possibly for this reason, although it was found possible to prepare *indoxylacetic acid*,†

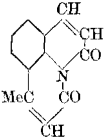
* In view of von Braun and Reutter's work, it is necessary to point out that this work was completed in 1924, that all the considerations here advanced were embodied in a thesis presented by one of us (J. G. J.) in that year for the degree of Doctor of Philosophy in the University of Sheffield, and that models and specimens thereof were on view at the British Empire Exhibition at Wembley in 1924.

† *During the performance of this portion of the work I was unable to exercise any supervision. The careful work involved is therefore to be credited to my collaborator.*—J. K.

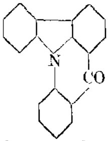


(XIII), after suitable revision of the procedure described in D.R.-P. 128955 (Friedlaender, " Fortschritte der Teerfarbenfabrikation," VI, p. 559), no satisfactory evidence of the formation of (III) could be obtained. In certain circumstances, detailed in the experimental portion of this paper, small quantities of a compound of the desired composition were obtained, but the *conditions were such as to make it necessary to regard this result as* not entirely conclusive.

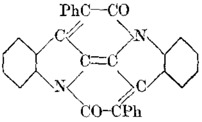
Although the outcome of the experimental work now described is thus in some respects indefinite, we venture to think that the mode of approaching the main problem on which it is based is not without value; for, if the benzene nucleus be regarded as a guide in the manner discussed, a scrutiny of the following formulæ of compounds described in the literature indicated under them will show it to be difficult to escape the conclusion that, if their respective constitutions have been correctly assigned, a plane distribution of groups round the nitrogen atom is probable.



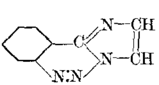
Reissert, *Ber.*, 1892, **25**, 108.



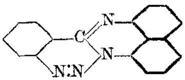
Eckert, Seidel, and Endler, *J. pr. Chem.*, 1922, **104**, 85.



Posner and Pyl, *Ber.*, 1923, **56**, 31; D.R.-P. 260243 (Friedlaender, *op. cit.*, XI, p. 293).

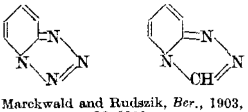


Balaban and King, J., 1925, **127**, 2704.

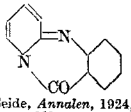


Sachse and Steiner, *Ber.*, 1909, **42**, 367.

If the same assumption be permissible in regard to the pyridine nucleus, the following compounds also should have plane configurations:



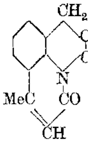
Marckwald and Rudszik, *Ber.*, 1903, **36**, 1111.



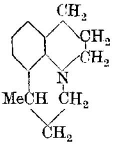
Seide, *Annalen*, 1924, **440**, 311.

In order, however, that a final conclusion may be reached it will be necessary to apply the usual tests for the asymmetry which would accompany non-planar configurations in any of these cases.

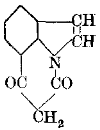
The considerations mentioned in connexion with the results of von Braun and Reutter indicate that the existence of the following compounds is less conclusive in respect of the question under discussion :



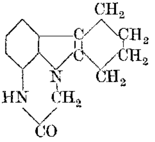
Reissert, *Ber.*, 1891, **24**, 841.



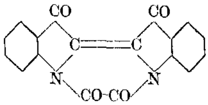
Reissert, *Ber.*, 1892, **25**, 118; Pinkus, *ibid.*, p. 2798; von Braun and Neumann, *ibid.*, 1919, **52**, 2015.



Bamberger and Steinitzki, *Ber.*, 1893, **26**, 1300; von Braun and others, *ibid.*, 1918, **51**, 1215.



Perkin and Riley, J., 1923, **123**, 2400.



Friedlaender and Sandes, *Ber.*, 1924, **57**, 641.

EXPERIMENTAL.

β-Phenylglutaric acid was prepared by hydrolysis of ethyl β-phenylpropane-ααγ-tricarboxylate with hydrobromic acid (b. p. 125°). The crude material (yield, 90%: Avery and Bouton, *Amer. Chem. J.*, 1898, **20**, 512, obtained only 70%), after crystallisation from dilute hydrochloric acid, gave a 75% yield of pure material, m. p. 139°.

1-*Ketohydrindene*-3-*acetic acid* (V) was produced when β-phenylglutaric acid (40 g.) was added rapidly, but in portions, to sulphuric acid (480 g.) at 150°. Immediate addition of the solution to cold water (2500 c.c.) caused the condensation product (30 g.) to separate in octagonal plates, completely soluble in sodium carbonate solution. Similarly, the material (1 g.) recovered by extraction of the mother-liquor with ether contained no purely ketonic substance. After crystallisation from benzene, the acid melted at 151° (Found :

C, 69·6; H, 5·2; equiv., 190. $C_{11}H_{10}O_3$ requires C, 69·6; H, 5·2%; equiv., 190).

The *semicarbazone* (Found: N, 17·0; equiv., 248. $C_{12}H_{13}O_3N_3$ requires N, 17·0%; equiv., 247) formed colourless, irregular prisms, m. p. 268° (decomp.). The *methyl* ester separated from benzene in large, hexagonal tablets, m. p. 65° (Found: C, 71·2; H, 6·0. $C_{12}H_{12}O_3$ *requires C, 70·6; H, 5·9%), and furnished a semicarbazone,* m. p. 152° (Found: N, 16·5. $C_{13}H_{13}O_3N_3$ requires N, 16·1%), and a 2-iso*nitroso*-derivative, m. p. 167° (decomp.) (Found: N, 6·2. $C_{12}H_{11}O_4N$ requires N, 6·0%). The last compound was prepared by adding hydrochloric acid (*d* 1·17; 0·5 c.c.) to a solution of the ester (3·2 g.) and freshly prepared amyl nitrite (2·5 g.) in methyl alcohol (102 c.c.) at 40°, and maintaining this temperature for 3 hours after the initial vigorous reaction had subsided.

The *ethyl* ester, a viscous liquid, b. p. 194—200°/13 mm. (Found: C, 72·0; H, 6·4. $C_{13}H_{14}O_3$ requires C, 71·6; H, 6·4%), similarly yielded a *semicarbazone*, m. p. 131—132° (Found: N, 15·2. $C_{14}H_{17}O_3N_3$ requires N, 15·2%), and a 2-iso*nitroso*-derivative, prisms, m. p. 193° (decomp.) (Found: N, 6·1. $C_{13}H_{13}O_4N$ requires N, 5·7%). When either the acid or the methyl ester was treated in ethyl-alcoholic solution with amyl nitrite and hydrochloric acid, the respective products melted at 192° (decomp.) (Found: N, 5·8, 5·9%) and at 193° (decomp.) (Found: N, 5·7%), and neither depressed the melting point of the derivative just described.

β-*Phenylglutaryl Chloride*.—The action of thionyl chloride, phosphorus pentachloride, or phosphorus trichloride upon the acid under the usual conditions led to the formation either of the well-known anhydride, m. p. 105° (Avery and Bouton, *loc. cit.*, p. 513; Vorländer, *Annalen*, 1901, **320**, 85), or of charred material, from which nothing definite could be isolated. An intimate mixture of the sodium salt (25 g.) with phosphorus pentachloride (40 g.) was therefore gently warmed for ½ hour after the initial reaction had subsided. The crude chloride (11 g.), b. p. 170—190°/15 mm., slowly deposited large plates, which melted at 46° after crystallisation from a mixture of carefully dried benzene and light petroleum. Owing to the facility with which the compound is converted into the anhydride, even on exposure to the atmosphere, the results of analysis were less satisfactory than usual (Found: Cl, 27·7; equiv., 62·5. $C_{11}H_{10}O_2Cl_2$ requires Cl, 28·9%; equiv., 61·2).

Action of Aluminium Chloride upon β-Phenylglutaryl Chloride.—Aluminium chloride (12 g.) was added to a solution of the crude chloride (9 g.) in light petroleum (100 c.c., b. p. 70—90°), which had been freed from aromatic componnds by treatment with nitrating acid, and finally the mixture was warmed until the evolution of

hydrogen chloride ceased. After the residue had been treated with ice, the light petroleum was volatilised in steam and shown not to have carried with it any of the products of reaction. These were extracted from the aqueous liquor by means of ether, and keto-hydrindeneacetic acid (3·1 g.) was removed from the extract by means of sodium carbonate solution and identified in the usual manner with that already described. The non-acidic material (1·1 g.) in the ethereal extract was a black tar, from which a gummy distillate (0·5 g.) was obtained by distillation under reduced pressure. No ketonic constituents could be detected in this by means of semicarbazide acetate.

When unpurified light petroleum was employed in an otherwise similar experiment, a ketonic substance was isolated. This was identical with that obtained when a mixture of purified light petroleum (90 c.c.) with benzene (3·2 g.) was employed as solvent. Under these conditions ketohydrindeneacetic acid (1 g.) and non-acidic material (2 g.) were obtained. The latter, after distillation under reduced pressure and crystallisation from benzene–light petroleum, furnished yellowish, hexagonal plates (1·15 g.), m. p. 78°. Its composition was in accord with the formula of *ω-3-hydrindonylacetophenone* (VII) (Found: C, 81·8, 82·1; H, 5·7, 5·5; *M*, ebullioscopic in benzene, 266. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%; *M*, 250). The *disemicarbazone*, hexagonal prisms, m. p. 233° (decomp.) (Found: N, 23·4. $C_{19}H_{20}O_2N_6$ requires N, 23·0%), and the *dioxime*, colourless prisms, m. p. 179° after dehydration (Found: Loss in weight at 130°, 8·5. $C_{17}H_{16}O_2N_2,1\frac{1}{2}H_2O$ requires H_2O, 8·8%. Found in the dried material: N, 10·0. $C_{17}H_{16}O_2N_2$ requires N, 10·0%), were prepared.

Anthranilodiacetic Acid (II).—The conditions of preparation described in D.R.-P. 128955 (Friedlaender, *op. cit.*, VI, p. 559) result in the formation of a large quantity of phenylglycine-*o*-carboxylic acid and only a small quantity of the desired acid. Vorländer and Mumme's method (*Ber.*, 1900, **33**, 3182) also is not very efficacious. Eventually a mixture of crystallised sodium carbonate (200 g.), water (1000 c.c.), anthranilic acid (60 g.), and chloroacetic acid (100 g.) was boiled for 8 hours, alkalinity being just maintained by suitable addition of sodium carbonate. Finally, the cooled deep green liquid was treated with 50% sulphuric acid (70 c.c.). The precipitate, together with the small amount obtained from the liquor after the addition of more acid (30 c.c.), furnished pure anthranilodiacetic acid (50 g.), m. p. 216° (decomp.) after crystallisation from water (400 c.c.). The material (40 g.) contained in the liquor from this crystallisation was chiefly phenylglycine-*o*-carboxylic acid, which was treated with more sodium chloroacetate.

The acid crystallised from water in colourless, octagonal plates, m. p. 216° (decomp.) (Vorländer and Mumme, *loc. cit.*, give 212°) [Found: equiv., 87. Calc. for $C_8H_8N(CO_2H)_3$: equiv., 84], and its solution in water or alcohol was not fluorescent. The blue fluorescence mentioned in D.R.-P. 128955 is due to phenylglycine-*o*-carboxylic acid, as are also the deep yellowish-brown colour of the acid there described and the dark red coloration it develops in not too dilute alcoholic solution on treatment with ferric chloride. Phenylglycine-*o*-carboxylic acid melts at 215° (decomp.), and a mixture of the two acids at about 200°.

Indoxylacetic Acid (XIII).—This acid is not obtainable by the process described in D.R.-P. 128955. In order to prepare it, anthranilodiacetic acid (16 g.) and a solution of sodium hydroxide (30 g.) in water (25 c.c.) were heated together with constant stirring. Apart from evolution of steam, no change occurred at 150°. At 200°, a few drops of water were added to facilitate disintegration of the hard lumps of material, and when this was complete and the mass of a uniform brown colour and of the consistency of clay, the mixture was allowed to cool. The solution of the cold melt (45 g.) in hot water (80 c.c.) furnished the crude acid on acidification with 50% sulphuric acid (60 c.c.). By crystallisation from hot water (100 c.c.), the pure acid (10 g.) was obtained in radiate clusters of monohydrated, hexagonal plates, which appeared green in the mass but yellow under the microscope (Found: loss in weight at 80°, 8·3. $C_{10}H_9O_3N,H_2O$ requires H_2O, 8·6%). The anhydrous acid melted at 165° (decomp.) (Found: C, 62·8, 63·2; H, 4·9, 5·0; N, 7·3. $C_{10}H_9O_3N$ requires C, 62·8; H, 4·7; N, 7·3%).

O-*Methylindoxylacetic Acid*.—A solution of indoxylacetic acid (5 g.) in 20% aqueous sodium hydroxide (6 c.c.) was gradually treated with methyl sulphate (8 g.) and a further quantity of alkali (14 c.c.). After being shaken for 3 days, the homogeneous light brown liquid yielded on acidification a reddish oil, which slowly solidified, and crystallised from aqueous methyl alcohol in monohydrated, colourless, hexagonal prisms (3·5 g.) (Found: loss in weight at 80°, 8·2, 8·4. $C_{11}H_{11}O_3N,H_2O$ requires H_2O, 8·1%), sparingly soluble in water, but easily soluble in sodium carbonate solution and in methyl and ethyl alcohols. The anhydrous acid melted at 141—142° and contained one methoxyl group [Found: C, 64·4; H, 5·5; N, 7·1; OMe, 15·5; equiv., 206. $C_9H_7N(OMe)\cdot CO_2H$ requires C, 64·4; H, 5·5; N, 6·8; OMe, 15·1%; equiv., 206].

Fusion of Sodium Indoxylactetate with Sodamide.—The sodium salt for this purpose was prepared as already described, with the exception that no water was added at 200°, but the mixture was thoroughly stirred and maintained at 200—210° for 2 minutes. In

order to prevent further reaction, the yellow, powdery mass was then quickly spread in a thin layer.

The interaction between this material and sodamide is very violent and the following procedure was finally adopted to secure some control of the reaction, and permit the use of sufficient condensing agent. Sodamide (40 g.) was melted and cooled until solidification commenced at about 150°. The crude salt (50—60 g.) from two of the fusions described above was then gradually added with continuous stirring. Finally, the temperature was carefully raised to 180—200°; then in spite of continuous stirring and cooling with cold water, a vigorous reaction occurred, accompanied by a strong odour of earbylamine and a further rise of temperature to 250°. When the main reaction had subsided and the temperature had been maintained at 220° for a further half-hour, the product was dissolved in hot water (200 c.c.) and acidified with 50% sulphuric acid (120 c.c.). In case the desired product, like indoxyl itself (compare Vorländer and Dresche, *Ber.*, 1902, **35**, 1701), might be unstable in presence of air, the tarry precipitate was dissolved in 20% sodium hydroxide solution (50 c.c.) and treated with methyl sulphate (20 c.c.). By repeated extraction with ether, a small quantity of material was obtained which crystallised from water in colourless needles (0·6 g.), m. p. 163°. Although this product could not be isolated unless the methylation process was carried out, its composition, remarkably enough, agreed with that of the compound sought in the experiment (Found: C, 63·8, 63·5, 63·1; H, 5·3, 5·5, 5·4; N, 14·7; *M*, by Rast's method, 210. $C_{10}H_{10}O_2N_2$ requires C, 63·2; H, 5·3; N, 14·7%; *M*, 190).

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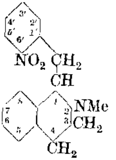
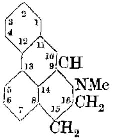
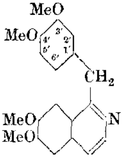
THE UNIVERSITY, SHEFFIELD. [*Received, June 27th*, 1927.]

LXXVII.—*Synthetical Experiments on the Aporphine Alkaloids. Part I. A Synthesis of* 5 : 6-*Dimethoxyaporphine.*

By JOHN MASSON GULLAND and ROBERT DOWNS HAWORTH.

IN attempts to synthesise aporphine alkaloids of type (II), the most usual starting points have been the substituted nitro*iso*quinolines of type (I), because these bases on reduction yield the corre-

sponding 2′-amino-derivatives, which may be converted by Pschorr's method (*Ber.*, 1896, **29**, 496) into the aporphine bases.

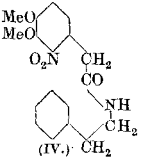
(I.)  (II.)   (III.)

The difficulty of preparing bases of type (I) has, however, until now precluded the synthesis of the naturally occurring alkaloids of type (II), with the exception of glaucine (Gadamer, *Arch. Pharm.*, 1911, **249**, 680) and dicentrine (Haworth, Perkin, and Rankin, J., 1925, **127**, 2018; 1926, 29). Both these alkaloids are exceptional in containing ethereal oxygen atoms in the 2 : 3-positions, and the necessary nitro*iso*quinoline bases are readily prepared by direct nitration of the requisite 1-benzyl*iso*quinoline derivative in which the 3′ : 4′-positions are occupied by methoxy-groups. Thus papaverine (III) readily yields 6′-nitropapaverine, which is convertible into glaucine (Pschorr, *Ber.*, 1904, **37**, 1926; Gadamer, *loc. cit.*). Many alkaloids of the aporphine group contain phenolic or ethereal oxygen in the 3 : 4-positions and in order to prepare bases of this constitution by the method of direct nitration it would be necessary to introduce a nitro-group into the 2′-position of a base of the papaverine type (III)—an operation which has not yet been accomplished.

The discovery by Hope and Robinson (J., 1911, **99**, 2114), that cotarnine and the allied pseudo-bases condense with derivatives of *o*-nitrotoluene, provided a new method for the preparation of bases of type (I). Gadamer, Oberlin, and Schoeler (*Arch. Pharm.*, 1925, **263**, 81) have employed this method for the synthesis of aporphine (II), but it has not yet been applied to the synthesis of the naturally occurring alkaloids of the series, partly owing to the inability of some pseudo-bases to condense with *o*-nitrotoluene derivatives and partly on account of the inactivity of the methyl group of 2-nitrohomoveratrole, as opposed to that of the 6-nitro-derivative. Derivatives of dinitrotoluene, however, readily condense with pseudo-bases (Hope and Robinson, *loc. cit.*; Graesser-Thomas, Gulland, and Robinson, J., 1926, 1971; Robinson and West, *ibid.*, p. 1985; Robinson and Shinoda, *ibid.*, p. 1987), but this modification introduces complications which greatly increase the practical difficulties in the preparation of bases of the 1-(2′-aminobenzyl)-2-

methyltetrahydro*iso*quinoline type (compare Robinson and Shinoda, *loc. cit.*).

A review of the literature convinced us that the well-known Bischler–Napieralski synthesis of *iso*quinoline bases had not been sufficiently investigated. From the observations made by Pictet and Kay (J., *1913*, **103**, 950) during an attempt to synthesise *apo*morphine dimethyl ether by a modification of this synthesis, it might be concluded that bases of type (I) cannot be prepared by this method. For example, these authors failed to obtain any basic material by the action of phosphorus pentoxide on 2′-nitro-3′ : 4′-dimethoxyphenylaceto-β-phenylethylamide (IV), and Gadamer, Oberlin, and Schoeler (*loc. cit.*) were unable to employ 2′-nitrophenylaceto-β-phenylethylamide in a synthesis of aporphine (II).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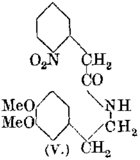
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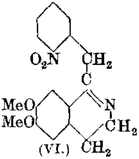
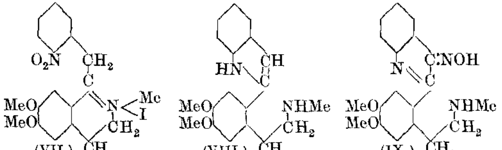

(VI.)

We have now achieved the stage of ring closure at which those attempted syntheses broke down, and as a preliminary case we have examined the action of a number of condensing agents on 2′-*nitrophenylaceto*-β-3 : 4-*dimethoxyphenylethylamide* (V). This amide was selected as being more favourable than the amide (IV), which Pictet and Kay investigated, because the activating influence of the methoxy-groups might be expected to facilitate *iso*quinoline formation. Treatment of the amide (V) with phosphorus pentoxide or phosphorus oxychloride under a variety of conditions did not produce any *iso*quinoline base. It was found, however, that 2′-*nitro*-6 : 7-*dimethoxy*-1-*benzyl*-3 : 4-*dihydroisoquinoline* (VI) was obtained in a yield of 90% by the action of phosphorus pentachloride on a cold chloroform solution of the amide (V). This orange-coloured, crystalline base (VI) yielded a pale yellow, crystalline *hydrochloride*, and the stability of the base is remarkable when it is remembered that 1-benzyl-3 : 4-dihydro*iso*quinoline bases readily undergo atmospheric oxidation (Buck, Haworth, and Perkin, J., 1924, **125**, 2176). The base (VI) readily yielded a sparingly soluble, pale yellow, crystalline *methiodide* (VII), the constitution of which was proved by fission with dilute sodium hydroxide solution in the manner described by Pschorr (*Ber.*, *1904*, **37**, *1932*). The products of this alkaline fission were *o*-nitrotoluene and 6 : 7-dimethoxy-2-methyl-

3 : 4-dihydro*iso*quinolone (Pyman, J., 1909, **95**, 1272; 1910, **97**, 269), the latter being identified by comparison with an authentic specimen which was presented to us by Dr. H. A. D. Jowett, on behalf of Burroughs Wellcome and Co., to whom we are greatly indebted.

When the methiodide (VII) was reduced with zinc dust and dilute sulphuric acid in *faintly* acid solution, a colourless, crystalline base, $C_{19}H_{22}O_2N_2$, m. p. 132°, was obtained which showed unexpected properties. The base was monoacidic; it formed a crystalline *monohydrochloride* on treatment with an excess of hydrochloric acid, and it was converted into a crystalline, non-basic *monoacetyl* derivative by the action of acetic anhydride. As a result of these and other observations, we have concluded that the substance $C_{19}H_{22}O_2N_2$ is 2-(4′ : 5′-*dimethoxy*-2′-β-*methylaminoethyl*)*phenylindole* (VIII). The presence of the indole nucleus was confirmed

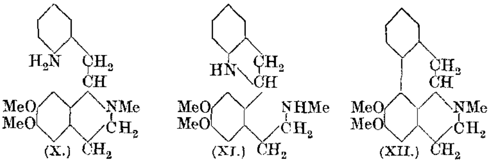


(VII.) (VIII.) (IX.)

by the positive colour reactions observed on testing with a pine shaving and with *p*-dimethylaminobenzaldehyde. On treatment with nitrous acid, the base, which did not diazotise, yielded a deep red solution, from which a colourless, crystalline compound, $C_{19}H_{21}O_3N_3$, has been isolated. We consider this compound to be the 3-*oximino*-derivative (IX), as it is soluble in sodium hydroxide and dissolves in dilute mineral acids with the production of a red colour, and this view is confirmed by the fact that the compound $C_{19}H_{21}O_3N_3$ does not give the Liebermann nitrosoamine reaction. We are at present unable to explain why the nitrous acid attacks the indole nucleus in preference to the basic methylamino-group.

When the methiodide (VII) was reduced with zinc dust and hydrochloric acid in *strongly* acid solution, a different product was obtained. This new base was an oil which yielded a crystalline *dihydrochloride*, and its *monoacetyl* derivative still possessed strongly basic properties. The base could be diazotised and showed the characteristic reactions of a primary aromatic amine, and there can be no doubt that it is 2′-*amino*-6 : 7-*dimethoxy*-1-*benzyl*-2-*methyltetrahydro*iso*quinoline* (X). A small quantity of an oily base, isomeric with (X), has been isolated from the mother-liquor of the

dihydrochloride of the base (X). This isomeric base, which gave a crystalline *dihydrochloride*, did not diazotise; it showed no indole colour reactions, but it yielded an oily *nitrosoamine* which gave the nitroso-reaction. We suggest that this base is 2-(4′ : 5′-*dimethoxy*-2′-β-*methylaminoethyl*)*phenyldihydroindole* (XI).



The base (X) was converted into 5 : 6-*dimethoxyaporphine* (XII), either (*a*) by diazotising it in 2*N*-sulphuric acid and adding copper powder, or (*b*) by diazotising it in a mixture of methyl alcohol and 2*N*-sulphuric acid and heating the solution on the water-bath. The yield of 5 : 6-dimethoxyaporphine was poor (10—15% of the theoretical), the chief by-products being the dilaudanosine derivative and the phenolic base, the former predominating in method (*a*) and the latter in method (*b*). 5 : 6-Dimethoxyaporphine is a crystalline base, m. p. 137°, which yields a sparingly soluble crystalline *hydrochloride* and a characteristic *methiodide*. A number of colour reactions are described in the experimental section.

We have obtained several substituted benzyl*iso*quinoline derivatives by the action of phosphorus pentachloride on amides analogous to (V), and we are using this method in the synthesis of the naturally occurring aporphine bases. *dl*-Bulbocapnine methyl ether has already been synthesised, and we hope to publish accounts of this and other researches at an early date.

Experimental.

o-Nitrophenylacetic acid (10 g.; prepared by a slight modification of Reissert's method, *Ber.*, 1897, **30**, 1030, potassium ethoxide being used instead of sodium ethoxide) in chloroform (150 c.c.) was gently refluxed with thionyl chloride (40 c.c.) for 1½ hours. The solvent was then removed by careful distillation under 13 mm. pressure, the liquid being occasionally warmed for a few minutes on the water-bath, with shaking. This procedure is necessary to avoid explosive decomposition of the *o*-nitrophenylacetyl chloride. The residual oil was used without further purification.

2′-Nitrophenylaceto-β-*3 : 4-dimethoxyphenylethylamide* (V).—*o*-Nitrophenylacetyl chloride (from 45 g. of acid), dissolved in benzene

(150 c.c.), was gradually added, with cooling and shaking, to β-veratrylethylamine (45 g.) in benzene (100 c.c.), and the slimy, buff-coloured precipitate was decomposed by the gradual addition of 10% sodium hydroxide solution. The amide (V), which separated from the benzene, was collected, combined with a small second crop, obtained by evaporating the benzene layer of the filtrate, and recrystallised from methyl alcohol, giving very pale buff-coloured, slender needles (73 g.), m. p. 112° (Found: C, 62·3; H, 5·9. $C_{18}H_{20}O_5N_2$ requires C, 62·8; H, 5·8%). The *amide* dissolves with sulphonation in concentrated sulphuric acid, giving an orange-coloured solution which is completely miscible with water. No basic material was isolated after the amide had been heated with phosphorus pentoxide or oxychloride in benzene, toluene, or xylene for various times; the products invariably consisted of unchanged amide and a brown, amorphous, non-basic material which could not be obtained in the crystalline condition. After a chloroform solution of the amide had been boiled with phosphorus pentachloride for 2 hours, a large amount of non-basic tar was isolated together with a very small amount of impure basic material.

2'-Nitro-6 : 7-dimethoxy-1-benzyl-3 : 4-dihydroisoquinoline (VI).—The amide (V) (4 g.) was mixed with a solution of phosphorus pentachloride (5 g.) in chloroform (30 c.c.) and kept for 24 hours at room temperature. The solvent was evaporated under reduced pressure from the crystalline material which had separated, the latter was extracted with boiling water and filtered from traces of tar, and the base (VI) was precipitated, by the addition of ammonia to the cooled filtrate, as an amorphous, pink solid which changed to a buff-coloured, crystalline solid after remaining in the liquor for several hours. The crude base crystallised from methyl alcohol in large, stout, orange, rhombic prisms (3·5 g.), m. p. 132°, which developed a deeper colour on heating to 100°, the colour reverting to orange on cooling (Found: C, 66·5; H, 5·7. $C_{18}H_{18}O_4N_2$ requires C, 66·3; H, 5·5%). The *hydrochloride*, pale yellow prisms, m. p. 228° (decomp.), was obtained by evaporating to dryness the pale yellow solution of the base in dilute hydrochloric acid and recrystallising the residue from absolute alcohol (Found: Cl, 9·7. $C_{18}H_{18}O_4N_2$,HCl requires Cl, 9·8%). The base dissolves in acetic anhydride, giving a pale yellow solution, and the absence of a deep green coloration indicates that spontaneous oxidation has not occurred (Buck, Haworth, and Perkin, *loc. cit.*).

2'-Nitro-6 : 7-dimethoxy-1-benzyl-3 : 4-dihydroisoquinoline methiodide (VII) may be prepared quantitatively (*a*) by heating a chloroform solution of the base (VI) and the calculated quantity of methyl iodide in a sealed tube at 100° for 4 hours, and (*b*) more con-

veniently by dissolving the base (VI) in an excess of warm methyl iodide, cooling the solution to room temperature, removing the excess of methyl iodide after 12 hours, and recrystallising the residue from rectified spirit. It forms pale sulphur-yellow needles, m. p. 208°, which are sparingly soluble in water and absolute alcohol (Found: C, 49·0; H, 4·7. $C_{19}H_{21}O_4N_2I$ requires C, 48·7; H, 4·5%). When ammonia was added to an aqueous solution of the methiodide, a deep red solution was obtained from which an ether-soluble, red, amorphous solid was precipitated; this redissolved on addition of water.

Alkaline fission. The methiodide (2 g.) was boiled with 3% sodium hydroxide solution (20 c.c.) for ½ hour, and the product was distilled in steam until the distillate was no longer turbid. From this, ether extracted *o*-nitrotoluene, which was reduced to *o*-toluidine (acetyl and *m*-nitrobenzoyl derivatives, m. p. 110° and 150°, respectively). The non-volatile residue from the steam distillation was evaporated to dryness; from the residual oil, chloroform extracted 6 : 7-dimethoxy-2-methyl-3 : 4-dihydro*iso*quinolone, which crystallised from benzene in colourless prisms, m. p. 124—125° (compare Pyman, *loc. cit.*), and was identified by comparison with an authentic specimen.

2-(4′ : 5′-*Dimethoxy-2′-β-methylaminoethyl)phenylindole* (VIII).—A solution of the methiodide (VII) (2 g.) in hot methyl alcohol (30 c.c.) was treated with zinc dust (6 g.) and heated on the water-bath while 10% sulphuric acid was added gradually. The methyl alcohol was allowed to evaporate, and the cooled, filtered solution was made alkaline with ammonia and extracted with ether. The extract was dried with sodium sulphate, the solvent removed, and the crystalline residue recrystallised from a little absolute ethyl alcohol. The *indole* derivative (VIII) separated with solvent of crystallisation in colourless, slender prisms (1 g.) which melted at 85°, resolidified, and remelted at 132° (Found: loss at 90°, 12·7. $C_{19}H_{22}O_2N_2,C_2H_5{\cdot}OH$ requires loss, 12·8%. Found in material dried at 90°: C, 73·5; H, 7·4. $C_{19}H_{22}O_2N_2$ requires C, 73·5; H, 7·3%). This substance does not give the carbylamine reaction, but it shows characteristic indole reactions, *e.g.*, a violet coloration in the pine-shaving test and a deep pink coloration in dilute hydrochloric acid on treatment with *p*-dimethylaminobenzaldehyde hydrochloride. The *hydrochloride* separated from a concentrated solution of the base (VIII) in ethyl-alcoholic hydrogen chloride in colourless, slender needles, which retained alcohol of crystallisation, melted at about 105°, resolidified, and remelted at a higher but somewhat indefinite temperature (Found in air-dried material: loss at 100°, 9·5; Cl, 9·0. $C_{19}H_{22}O_2N_2,HCl,C_2H_5{\cdot}OH$ requires loss, 11·7;

Cl, 9·0%. Found in material dried at 100° : C, 65·6; H, 6·7. $C_{19}H_{22}O_2N_2$.HCl requires C, 65·8; H, 6·6%). The *monoacetyl* derivative separated as a white solid when an excess of acetic anhydride was allowed to react with a benzene solution of the base (VIII) for 3 days at room temperature. The mixture was shaken with ammonia, the solid collected, and a further quantity obtained by concentration of the benzene layer of the filtrate. The acetyl derivative crystallised from methyl alcohol, in which it was moderately easily soluble, in small prisms, m. p. 138° (Found : C, 71·4; H, 6·8. $C_{21}H_{24}O_3N_2$ requires C, 71·6; H, 6·8%). It is quite devoid of basic properties and resists hydrolysis by dilute aqueous acids and alkalis.

2-(4′ : 5′-*Dimethoxy-2′-β-methylaminoethyl)phenyl-3-oximinoindole* (IX).—When the base (VIII) was dissolved in dilute hydrochloric acid and treated with sodium nitrite, a deep blood-red solution was obtained, the colour of which was not destroyed by boiling. The solution contained no diazonium salt, since no azo-dye was precipitated on adding it to an alkaline solution of β-naphthol. Before the nature of the base (VIII) was established, an attempt was made to bring about the Pschorr reaction, and the *oximino*-derivative (IX) was isolated from the experiment. The hydrochloride (0·2 g.) of the base (VIII), dissolved in 2*N*-sulphuric acid (5 c.c.) and methyl alcohol (5 c.c.), was diazotised below 0° by the gradual addition of the calculated quantity of *N*/20-sodium nitrite (freshly standardised); water (10 c.c.) was added, the solution warmed on the water-bath for 30—40 minutes, cooled, made alkaline with sodium hydroxide, and the slight precipitate extracted twice with ether. The extract was washed with water and dried with potassium carbonate, and the solvent removed; the residual yellow gum deposited colourless needles, m. p. 177—178°, after rubbing with warm ethyl alcohol. A much larger quantity of the oximino-derivative (IX) was obtained by adding solid ammonium chloride to the sodium hydroxide solution, and extracting the colourless solid precipitate with much ether. The extract, which showed a magnificent blue fluorescence, was dried with potassium carbonate, and concentrated until the solution was filled with a mass of colourless needles, m. p. 178° (Found : C, 67·0; H, 6·5. $C_{19}H_{21}O_3N_3$ requires C, 67·2; H, 6·2%). The oximino-compound (IX) is sparingly soluble in ether or ethyl alcohol. It dissolves in dilute hydrochloric acid to a strawberry-coloured solution, and slowly in sodium hydroxide, giving a pale yellow solution, from which it is precipitated by the addition of ammonium chloride. With phenol and concentrated sulphuric acid a yellow coloration was observed, but the characteristic nitroso-reaction was absent.

2′-Amino-6 : 7-dimethoxy-1-benzyl-2-methyltetrahydroisoquinoline (X).—The methiodide (VII) (8 g.), suspended in hot water (80 c.c.) and concentrated hydrochloric acid (160 c.c.), was gradually treated with zinc dust (25 g.) with vigorous shaking. The liquid was filtered, made alkaline with ammonia, cooled, and extracted with ether, the extract dried with sodium sulphate, and the solvent removed. The *base* (X) remained as an oil which could not be crystallised. The *dihydrochloride* was prepared by treating the base with alcoholic hydrogen chloride; it was readily soluble in water, but very sparingly soluble in absolute alcohol, from which it separated in small, colourless prisms, m. p. 243—244° (decomp.) (Found: C, 59·3; H, 6·7. $C_{19}H_{24}O_2N_2,2HCl$ requires C, 59·2; H, 6·7%). A solution of the dihydrochloride, when diazotised, formed a pale orange-coloured solution, which deposited a crimson azo-dye on being poured into an alkaline solution of β-naphthol; the dye dissolved in concentrated sulphuric acid, producing an intense magenta solution. The *monoacetyl* derivative was prepared by the action of the calculated amount of acetic anhydride on an ethereal solution of the base (X). After 2 hours, the acetate which separated was decomposed with ammonia, and the ether removed in a current of air; the acetyl derivative crystallised from methyl alcohol in splendid, colourless prisms, m. p. 153—154° (Found: C, 71·1; H, 7·5. $C_{21}H_{26}O_3N_2$ requires C, 71·1; H, 7·5%). This acetyl derivative is basic; it dissolves in cold dilute hydrochloric acid to a colourless solution, from which it is precipitated by the addition of alkali.

2-(4′ : 5′-Dimethoxy-2′-β-methylaminoethyl)phenyldihydroindole (XI).—The *dihydrochloride* of this base gradually separated from the alcoholic hydrogen chloride mother-liquor from which the dihydrochloride of the base (X) had crystallised. It separated from ethyl alcohol, in which it was readily soluble, in colourless prisms which softened slightly at 180° and melted with evolution of gas but no darkening at 186° (Found in material dried at 100°: C, 59·2; H, 6·8. $C_{19}H_{24}O_2N_2,2HCl$ requires C, 59·2; H, 6·7%). The *base* was liberated as an oil by the addition of sodium hydroxide to an aqueous solution of the hydrochloride. It gave no coloration with a pine shaving or with *p*-dimethylaminobenzaldehyde. The addition of sodium nitrite to a solution of the dihydrochloride in dilute sulphuric acid produced a pale yellow solution which did not couple with alkaline β-naphthol. From the solution, basified with ammonia, ether extracted a *nitrosoamine*, a light brown oil which gave the Liebermann nitroso-reaction. The nitroso-group is probably connected to the methylamino-group, as we were unable to isolate a migration product by the action of alcoholic hydrogen chloride.

5 : 6-*Dimethoxyaporphine* (XII).—(*a*) A mechanically stirred solution of the base (X) (from 7·5 g. of dihydrochloride) in 2*N*-sulphuric acid (30 c.c.) was mixed with ice (60 g.) and diazotised by the calculated amount of 2*N*-sodium nitrite (freshly standardised). Copper powder (3 g.) was added to the orange-coloured solution, nitrogen was evolved, and after 6 hours the filtered mixture was reduced with zinc dust (3 g.) and concentrated hydrochloric acid (10 c.c.), and again filtered. The filtrate was made alkaline with ammonia, and thoroughly extracted with ether. Objectionable emulsions, which often made filtration necessary, were produced at this stage, since large quantities of the dilaudanosine derivative separated as a brown amorphous powder. The ethereal extract was washed with sodium hydroxide to remove a small amount of phenolic base, dried with sodium sulphate, and concentrated, and the brown, oily residue mixed with 50% hydrochloric acid (30 c.c.). After 12 hours, the *hydrochloride* of 5 : 6-dimethoxyaporphine (XII) was collected, washed with 50% hydrochloric acid, and recrystallised from hot water (yield 0·7 g.).

(*b*) The dihydrochloride (8 g.) of the base (X) in 2*N*-sulphuric acid (40 c.c.) and methyl alcohol (40 c.c.) was cooled below 0° and treated with the calculated amount of 2*N*-sodium nitrite. The orange-coloured solution was heated on the water-bath for ½ hour, reduced with zinc (4 g.) and concentrated hydrochloric acid (12 c.c.), and filtered, and the pale yellow solution was made alkaline with ammonia and extracted with ether. No dilaudanosine derivative was precipitated, but a large amount of phenolic base was removed by washing the ethereal extract with sodium hydroxide. The ether was dried with sodium sulphate and evaporated, 50% hydrochloric acid (30 c.c.) was added to the residual brown oil, and the hydrochloride (1·2 g.) was isolated as described above in method (*a*). 5 : 6-*Dimethoxyaporphine* (XII) was precipitated by the addition of sodium hydroxide to an aqueous solution of the hydrochloride. The oil, which rapidly hardened, was extracted with ether, the extract dried with sodium sulphate, and the solvent removed until 5 : 6-dimethoxyaporphine began to separate in colourless, large, stout, rhombic prisms, m. p. 136—137° (Found: C, 77·1; H, 7·1. $C_{19}H_{21}O_2N$ requires C, 77·3; H, 7·2%). The base gives a colourless solution in concentrated sulphuric acid, a pinkish-purple coloration with Erdmann's reagent, a deep bluish-purple with Frohde's reagent, and a green coloration, which rapidly turns brown, with Mandelin's reagent. The *hydrochloride* is sparingly soluble in water, from which it separates in colourless, small prisms, m. p. 258° (decomp.) (Found: C, 68·8; H, 6·6; Cl, 10·7. $C_{19}H_{21}O_2N$,HCl requires C, 68·8; H, 6·6; Cl, 10·7%). The *methiodide* was prepared by reflux-

ing the base (XII) for a few minutes with an excess of methyl iodide; the excess of methyl iodide was removed, and the solid residue recrystallised from absolute alcohol, from which the methiodide separated in magnificent, colourless, hexagonal plates, m. p. 223° (Found: C, 55·0; H, 5·5. $C_{20}H_{24}O_2NI$ requires C, 54·9; H, 5·5%).

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LXXVIII.—*The Acetoacetic Ester Condensation.*

By MERVIN CLARENCE FRANKLIN and WALLACE FRANK SHORT.

IN 1922 the whole question of the mechanism of the acetoacetic ester condensation was reopened by Scheibler and Ziegner (*Ber.*, **55**, 789), who stated that the product of the action of sodium or of sodamide upon ethyl acetate (subsequently referred to as the "final product" in the present paper) is not ethyl sodioacetoacetate but a derivative of orthoacetoacetic acid of the structure (I). The mechanism of the reaction was considered to be as follows:

$$CH_3{\cdot}CO_2Et \xrightarrow{Na\ or\ NaNH_2} CH_2{:}C(ONa){\cdot}OEt \xrightarrow{CH_3{\cdot}CO_2Et} CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(ONa)(OEt)_2 \quad (I.)$$

and the ortho-ester structure was assigned to the final product essentially as a result of the observation that it is decomposed by water with formation of keten acetal in 16% yield according to the equation

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(ONa)(OEt)_2 \longrightarrow CH_3{\cdot}CO_2Na + CH_2{:}C(OEt)_2.$$

Scheibler and Friese (*Annalen*, 1925, **445**, 143) found that the "final product" reacts with benzaldehyde to produce cinnamic ester, whereas ethyl sodioacetoacetate is without action upon benzaldehyde under the same experimental conditions. Since cinnamic ester is produced by the interaction of sodium, ethyl acetate, and benzaldehyde (Claisen's cinnamic ester synthesis), the "final product" was stated to be a kind of molecular complex in which the ester enolate fragment, $CH_2{:}C(ONa){\cdot}OEt$, has a certain independence.

The structure (I) has been criticised by Adickes (*Ber.*, 1926, **59**,

2522) on the ground that such a substance would readily decompose into ethyl sodioacetoacetate and alcohol and moreover that the formation of such an additive compound of sodium ethoxide and acetoacetic ester would be an exception to the regularities which he had established between the structure of esters and their ability to form addition compounds with sodium ethoxide (*Ber.*, 1925, **58**, 1992; 1926, **59**, 2522; 1927, **60**, 272).

The mechanism of the reaction advanced by Scheibler also appears to be incapable of explaining the fact that only esters containing two α-hydrogen atoms undergo the acetoacetic ester condensation smoothly. Scheibler and Friese (*loc. cit.*, p. 149) assert that *iso*butyric ester undergoes slow and incomplete " self condensation " in the presence of sodium ethoxide, as may be recognised by the formation of the keten acetal when the product is decomposed with water, but state that the product " cannot yield a compound analogous to ethyl sodioacetoacetate by further loss of alcohol." This explanation appears to be inadequate, because there seems to be no reason why $CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}C(ONa)(OEt)_2$ should be incapable of hydrolysis in presence of acids to $CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$ in the same way that (I) passes into acetoacetic ester. Moreover, the experiments of Dieckmann (*Ber.*, 1900, **33**, 2670) on the reversibility of the acetoacetic ester condensation are difficult to reconcile with the new mechanism.

We have prepared the " final product " of the acetoacetic ester condensation by the action both of sodium and of sodamide upon highly purified ethyl acetate, and have condensed it with a variety of alkyl and acyl halides. By using sodamide, Scheibler and Ziegner (*loc. cit.*) obtained the " final product " in 94% yield and stated that it is less contaminated with impurities than the product obtained by the action of sodium. The largest yield obtained by us by repeating this preparation under the prescribed condition was approximately 60% and the product contained both sodium acetate and sodium acetamide (40—50%), as was shown by analysis and by an examination of the products formed on condensation with benzyl chloride, etc. Titherley (J., 1902, **81**, 1520) found that much sodium acetate and sodium acetamide are produced by the action of sodamide upon ethyl acetate and Freund and Speyer (*Ber.*, 1902, **35**, 2321) obtained a very small yield of acetoacetic ester (16%, calculated on the ethyl acetate, or 8·4%, calculated on the sodamide) by this method of preparation. The sodium acetate is probably produced by the saponification of ethyl acetate by sodium ethoxide (compare Geuther, *Jahresber.*, 1868, 513) produced in secondary reactions (compare Oppenheim and Precht, *Ber.*, 1877, **9**, 320; Scheibler, Ziegner, and Peffer, *Ber.*, 1922, **55**, 3921).

If the " final product " has the structure (I), it is to be anticipated that its condensation with alkyl halides would result in the formation of an ortho-ester, whereas if it is a molecular compound (II) in which the fragment $CH_2:C(OEt)\cdot ONa$ has a sufficient independence, *C*-substitution should occur and ethyl acetate should be liberated (compare Scheibler, Marhenkel, and Bassanoff, *Ber.*, 1925, **58**, 1198):

$$\text{(II.)} \left\{\begin{matrix} CH_2:C(OEt)\cdot ONa \\ CH_3\cdot CO_2Et \end{matrix}\right\} + RCl \longrightarrow \begin{matrix} R\cdot CH_2\cdot CO_2Et \\ + \\ CH_3\cdot CO_2Et \end{matrix}.$$

Frankland and Duppa (*Phil. Trans.*, 1866, **156**, 37) condensed the " final product " with various alkyl halides, but unfortunately added water before distillation of the product, so that the mono- and di-alkylacetic esters which they obtained might have been formed by the " acid fission " of the corresponding acetoacetic esters. Seseman (*Ber.*, 1873, **6**, 1086), however, obtained mono- and di-benzylacetic acids by saponification of the substance produced by the condensation of the " final product " with benzyl chloride and assumed that mono- and di-benzylacetic esters were formed in the primary reaction. We find that neither of these esters is present and that the product contains benzyl- and dibenzyl-acetoacetic esters together with benzyl acetate and that acetobenzylamide * is formed in addition when sodamide is used instead of sodium for the preparation of the " final product." In no case have we detected the formation of either ortho-esters or *C*-substituted acetic esters when the " final product " is condensed with alkyl or acyl halides (butyl iodide and benzoyl chloride in addition to those mentioned in this paper), and the products are substantially those which would be formed from a mixture of ethyl sodioaceto-acetate with sodium acetate (and sodium acetamide when sodamide is used in the preparation).

When the dry " final product " is heated, it begins to decompose at about 130° with distillation of a small quantity of ethyl alcohol, ethyl acetate, and a trace of acetone. On the other hand, it reacts with ethyl iodide below 100° to form ethyl ethylacetoacetate. The results obtained point to the conclusion that " the final product " is very easily transformed into ethyl sodioacetoacetate even if this substance is not already present in it. The formation of keten acetal and the ability of the " final product " (unlike ethyl sodio-acetoacetate) to condense with benzaldehyde constitute the only

* The formation of acetobenzylamide (68% yield, calculated on the sodium acetamide present) was unexpected, since Titherley (J., 1901, **79**, 391) states that substituted amides are not formed by the action of alkyl halides on sodium acetamide. We are investigating this reaction further.

evidence available at present in favour of the structure assigned to it by Scheibler. Since keten acetal is produced in so small a yield and the "final product" is never approximately homogeneous, the formation of the acetal may be the result of a secondary reaction. We have not made investigations in this region because Scheibler (*Annalen*, 1925, **445**, 150, *footnote*) is investigating the keten acetals. We find that ethyl sodioacetoacetate reacts with benzaldehyde with considerable violence, and this reaction will be discussed in a subsequent communication.

EXPERIMENTAL.

The ethyl acetate employed was purified first by Roberts's modification (*J. Soc. Chem. Ind.*, 1924, **43**, 296T) of Wade's method (J., 1905, **87**, 1656) and finally by digestion with phosphorus pentoxide (Perkin, J., 1884, **45**, 491; Inglis and Knight, P., 1907, **23**, 198). It boiled at 76·7—77·2°/760 mm. The ether employed in the preparation of the "final product" was carefully freed from alcohol and moisture, and all the reagents were dried before use. Precautions were taken in all the experiments to prevent the absorption of moisture.

Preparation of the "Final Product" from Sodamide.—The prescriptions of Scheibler and Ziegner (*Ber.*, 1922, **55**, 801) were followed exactly and 65 g. and 73 g. of the dry product were obtained from portions of 150 g. of ethyl acetate. Small portions of the product were extracted with ether (in an atmosphere of dry hydrogen) to remove traces of acetamide, and the residue was freed from ether at 40° in a vacuum [Found: Na, 22·7, 21·5; N, 41·4, 31·4 in the respective preparations. Calc. for $CH_3{\cdot}CO{\cdot}CH_2{\cdot}C(ONa)(OEt)_2$: Na, 11·6%. Calc. for $CH_3{\cdot}C(ONa){:}CH{\cdot}CO_2Et$: Na, 15·1%].

Action of Heat upon the "Final Product" obtained by the Action of Sodium.—When the dry "final product" (100 g.) was heated, a liquid began to distil at about 130° and the residue became dark brown. The decomposition appeared to be complete at about 190° and the distillate (20 g.) on fractionation yielded ethyl acetate, alcohol, and a trace of acetone. It did not immediately decolorise dilute alkaline permanganate, so that keten acetal was probably absent (compare Scheibler and Ziegner, *loc. cit.*).

Condensation of Benzyl Chloride with the "Final Product" prepared from Sodium.—The "final product" (67 g.) was heated at 200° with benzyl chloride (150 g.: 77·5 g. in excess of the amount equivalent to the sodium present) until the mixture was no longer alkaline (7·5 hours). Sodium chloride was removed from the dark red liquid and was washed with purified ether, the washings being added to the red liquid. The ether was removed on the water-bath

and the residue yielded the following initial fractions when distilled at 15 mm.: (1) 70—90° (60 g.), (2) 90—100° (14 g.), (3) 100—120° (20 g.), (4) 120—127° (12 g., partly solid), (5) 127—190° (29·5 g., mostly solid), (6) 190—197° (13 g.), (7) 197—240° (7 g.), (8) residue (2—3 g., mainly sodium chloride). Systematic refractionation and purification yielded benzyl chloride, benzyl acetate (21 g. Equiv. by saponification, 147·9. Calc., 150), acetamide, acetobenzylamide (m. p. 60—60·5°; identified by conversion into benzylamine hydrochloride, m. p. 248°), and αα-dibenzylacetoacetic ester (0·8 g.; identified by conversion into dibenzylacetic acid, m. p. 89·5—90°). No α-benzylacetoacetic ester was isolated and none of the fractions gave a coloration with ferric chloride solution.

Condensations with the "Final Product" prepared from Sodium.—(1) *With ethyl iodide.* Ethyl iodide (b. p. 71·3—72·3°; 200 g.) was heated on the water-bath with the dry "final product" (181 g.) until the mixture was no longer alkaline (9 hours). The sodium iodide was filtered off and extracted with purified ether, the extract being added to the filtrate. Systematic fractionation of the product yielded ethyl iodide (11 g.), ethyl acetate (19 g.), and ethyl ethylacetoacetate (96 g.). Sodium iodide and a viscous oil remained in the distilling flask, but no diethylacetoacetic ester could be isolated from it by extraction with ether and subsequent distillation.

(2) *With benzyl chloride.* The "final product" (135 g.) was condensed with benzyl chloride (177·5 g.: 40 g. in excess of the amount equivalent to the sodium present) under the conditions previously described and the product was worked up in the same way. The initial fractions obtained at 15 mm. were: (1) 78—85° (45·5 g.), (2) 85—130° (32 g.), (3) 130—175° (64 g.), (4) 175—220° (12 g.), (5) 220—240° (35·5 g.), (6) residue (2—3 g.). Systematic refractionation yielded benzyl chloride, benzyl acetate (b. p. 101—105°/15 mm. Equiv. by saponification, 168. Calc., 150. Identified by saponification to benzyl alcohol and oxidation to benzoic acid), α-benzylacetoacetic ester (b. p. 165·2°/15 mm.), and αα-dibenzylacetoacetic ester (m. p. 56°).

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LXXIX.—*Lead Subacetate Solution ("Goulard's Extract") and its Reaction with Phenols.*

By Charles Stanley Gibson and Ernest Matthews.

During experiments on the production of easily isolable lead organic compounds with a view to their possible use as therapeutic agents, it has been necessary to investigate the precipitates which phenols produce with the aqueous solution of lead subacetate known in pharmacy as Goulard's extract.

This solution is referred to under that name in the 1898 and 1914 editions of the British Pharmacopœia, although the method of preparing it, by boiling 250 g. of lead acetate and 175 g. of powdered lead oxide with water, filtering the solution from the considerable residue, and making up the cooled filtrate to 1 litre, was described in all editions of the Pharmacopœia from 1867 to 1898 inclusive. In the editions of 1867, 1874, and 1885, a formula was given for the lead subacetate, but no formula was given in the later editions. Although the essential properties of the solution appear to be the same as formerly, the method of making Goulard's extract in the 1914 edition is different from that previously described and is set forth in the experimental portion of the present paper. It has now been possible to prove that the composition of the solute is $Pb(OH)_2,Pb(O_2C{\cdot}CH_3)_2$ or $Pb(OH)(O_2C{\cdot}CH_3)$, agreeing with the formula $Pb_2O(C_2H_3O_2)_2$ given in the 1885 edition. If, instead of taking the above quantities of lead acetate and lead oxide—which are in approximately equivalent proportion—three times the amount of lead oxide is taken, the composition of the solute is $2Pb(OH)_2,Pb(O_2C{\cdot}CH_3)_2$, thus confirming the existence in solution of the two definitely established basic acetates of lead. Further, a volumetric method of standardisation of Goulard's extract is shown to be possible and an improvement on that described in the Pharmacopœia.

It appears that Medley (*Pharm. J.*, 1926, 149) was the first to point out that an aqueous solution of phenol yields a precipitate with a solution of lead subacetate but not with a solution of lead acetate. Medley stated that the fine white powder was readily soluble in alcohol (50%), acetone, benzene, chloroform, ether, and dilute acetic acid. He concluded that the precipitate was lead phenoxide, $(C_6H_5{\cdot}O)_2Pb$, and if this were so, it would be identical with the compound prepared by dissolving lead oxide in hot phenol (Calvert, J., 1865, **18**, 69). Further, he found that twelve other phenols reacted similarly; in only one case (pyrogallol) was the

precipitate insoluble in acetic acid and in the majority of cases the precipitate was soluble in chloroform.

In the present paper, three typical compounds are described in detail, *viz.*, the precipitates produced with phenol, *o*-nitrophenol, and *o*-bromophenol. Others have been investigated, but not so completely, since it has been found that, although the precipitates as soon as they are formed and while still in contact with the solution may be soluble in organic solvents, they cease to be soluble to anything like the desired extent after separation, washing, and drying at the ordinary temperature. The formation of these precipitates is apparently general, but the sparing solubility in water of many phenols renders the experimental difficulties somewhat greater than might be anticipated.

The composition of these precipitates appears to be $Pb(OR)_2,Pb(OH)(O_2C\cdot CH_3)$, where R = an aryl or substituted aryl group. These formulæ have been determined by careful analyses, but, unfortunately, molecular-weight determinations have not been found practicable. The presence of the acetic acid residue was always detected by the usual test. The only previously described compounds with which these substances can be compared are the sparingly soluble compounds, $Pb(OH)(O\cdot C_6H_4\cdot NO_2)$, prepared by Post and Mehrtens (*Ber.*, 1875, **8**, 1552) by mixing dilute aqueous solutions of lead acetate and the potassium salts of *o*-, *m*-, and *p*-nitrophenols.

EXPERIMENTAL.

The Solute in Goulard's Extract.—The Liquor Plumbi Subacetatis Fortis (Strong Solution of Lead Subacetate—Goulard's Extract) is made (British Pharmacopœia, 1914, 229) by dissolving 250 g. of lead acetate in 750 millilitres * of distilled water, adding 175 g. of powdered lead oxide, setting the mixture aside for 48 hours and shaking it occasionally; the solution is filtered and sufficient distilled water is passed through the filter to produce 1000 millilitres. The following are the stated characteristics of the solution: "A clear colourless liquid, with a sweet astringent taste; alkaline to litmus. Becomes turbid by exposure to the air. Forms an opaque, white jelly with mucilage of gum acacia. Yields the reactions characteristic of lead and of acetates. Specific gravity 1·275. When 1 gramme is diluted with 20 millilitres of water and mixed with excess of *N*-solution of oxalic acid, the precipitate collected,

* 1 Millilitre (ml.) = vol. at 4° of 1 g. of water. The term "millilitre" (without definition) was given in the 1867 edition of the British Pharmacopœia in the metrical system of measures of capacity. In the present work, the unit of volume employed is the c.c., = 0·001 litre at 15°.

washed, transferred to a flask, and decomposed with excess of diluted sulphuric acid, the mixture thus obtained, heated to 60°, decolorises not less than 17 millilitres of *N*/10-solution of potassium permanganate."

The solution made by shaking mechanically for 8 hours lead acetate (250 g.), lead oxide (175 g.), and water (750 c.c.), filtering the liquid from the very considerable quantity of white precipitate, and making the filtrate up to 1 litre had a specific gravity of 1·283 at 13°, and 1 g. of the solution, treated as described above, decolorised 20·5 c.c. of 0·1*N*-potassium permanganate. The solution is conveniently preserved and delivered from an apparatus similar to that employed for an aqueous solution of barium hydroxide. Under these conditions it keeps almost indefinitely and there is little difficulty in obtaining a clear liquid. For most of the present work, the solution prepared from the above quantities was made up to 2 litres with distilled water.

When the solution was evaporated under reduced pressure at the ordinary temperature, a solid product was obtained of which the analytical figures approximated to the formula $Pb(OH)_2,Pb(O_2C{\cdot}CH_3)_2$ or $Pb(OH)(O_2C{\cdot}CH_3)$, but, from its appearance, there was considerable doubt as to its purity. The solution can be titrated against nitric acid or acetic acid and a fairly good end-point obtained, bromcresol-purple being used as indicator, and from this a method of standardisation of the solution can be developed. By using standard acetic acid and carrying out the titration in Nessler tubes, the end-point being determined colorimetrically, the following results were obtained with 5·0 c.c. of the solution: Pb present as $Pb(OH)_2$, by titration, 0·3070 g. Total Pb present, determined as $PbSO_4$, 0·5870 g. Hence Pb present as $Pb(O_2C{\cdot}CH_3)_2$, 0·2800 g. Therefore the molecular proportion of lead hydroxide and lead acetate is 1·0 : 0·91.

This result is obviously subject to error due to hydrolysis of the lead acetate in solution, which was partly corrected as follows: By titrating the solution against a known volume of standard acetic acid, the total amount of lead hydroxide in the solution can be calculated and, by using the above result, the total weight of lead acetate in the neutralised solution can be estimated approximately. This weight of lead acetate was then dissolved in a known volume of standard acetic acid and titrated back to neutrality with a standard aqueous solution of sodium hydroxide. (Any error due to hydrolysis of sodium acetate will be small compared with that of lead acetate.) From the results so obtained, it is possible to calculate the amount of acetic acid necessary to suppress the hydrolysis of the lead acetate; and on applying this correction

the molecular proportion of lead hydroxide to lead acetate in the solution becomes 1 : 1·01.

Additional confirmation of this result was obtained by the following method. A standard solution of hydrochloric acid (50 c.c.) was boiled and 6·0 c.c. of the basic lead acetate solution were added, followed by an excess of an aqueous solution of sodium sulphate. To the cooled solution, neutral ethyl alcohol (20 c.c.) was added, and the resulting mixture titrated with standard sodium hydroxide solution. The following results were obtained: Pb as $Pb(OH)_2$, 0·3583 g. Total Pb, determined as $PbSO_4$, 0·7042 g. (mean of 0·7026, 0·7020, and 0·7080). Hence Pb as $Pb(O_2C{\cdot}CH_3)_2$, 0·3459 g., and the molecular proportion of lead hydroxide to lead acetate is 1·0 : 0·97. Allowing for experimental error, these results strongly indicate the nature of the solute as $Pb(OH)_2,Pb(O_2C{\cdot}CH_3)_2$.

The relative quantities of lead oxide and lead acetate used in making the Goulard's extract are in approximately molecular proportion. The residue from which the solution is filtered is an apparently homogeneous, white solid, which must contain lead hydroxide and lead acetate in approximately molecular proportion, probably as the solid basic acetate of lead of the above composition. A solution was made up as described above, lead oxide (52 g.) and lead acetate (25 g.), *i.e.*, 3 mols. of the former to 1 mol. of the latter substance, being used, and the following analytical figures were obtained when 5 c.c. of the solution were analysed by the second method described above: Pb as $Pb(OH)_2$, 0·3004 g. Total Pb, determined as $PbSO_4$, 0·4508 g. Hence Pb as $Pb(O_2C{\cdot}CH_3)_2$, 0·1504 g., and the molecular proportion of lead hydroxide to lead acetate in the solution is 1·998 : 1·000. This indicates the nature of the solute in this solution as being $2Pb(OH)_2,Pb(O_2C{\cdot}CH_3)_2$. The insoluble residue from which the solution was filtered in this case was certainly not homogeneous, unchanged lead oxide obviously being present.

Products of the Reaction between "Goulard's Extract" and Phenols.—In the first experiments, the precipitate produced on mixing the extract with an aqueous solution of phenol was immediately extracted with benzene or chloroform, and the extract was washed with water and dried with anhydrous sodium sulphate. The solvent was evaporated, but the substance did not separate until it was precipitated with ligroin. After drying in a vacuum desiccator over sulphuric acid or phosphorus pentoxide, the substance was found to be insoluble in the original solvent at the ordinary temperature, and although it was appreciably soluble in the warm solvent some decomposition always took place under these conditions. Products were obtained in this way from phenol, the

naphthols and nitrophenols, but duplicate analyses carried out on several preparations of these showed considerable variation in composition.

An apparatus was specially designed in which the reaction could be carried out, and the product filtered off and washed, in an atmosphere free from carbon dioxide. By its means, the action of "Goulard's Extract" on numerous phenols and their derivatives, *e.g.*, methyl salicylate and 3-nitro-4-hydroxyphenylarsinic acid (U.S. Pat. 1607299), has been examined and found to be of general application. The following may be regarded as typical:

Phenol compound. Phenol (6 g.), dissolved in water (150 c.c.) at 20°, was allowed to react with the solution (40 c.c.). The white precipitate was washed with water (200 c.c.) at 20°. (Hot water used for washing caused shrinkage and decomposition of the compound.) The compound is a white micro-crystalline powder which begins to melt at about 80° (decomp.) and then chars, leaving a deposit of lead and some lead oxide (PbO) (Found: C, 25·4, 25·4, 24·9; H, 2·0, 1·95, 2·0; Pb, 61·1, 61·8.* $C_{14}H_{14}O_5Pb_2$ requires C, 24·85; H, 2·1; Pb, 61·25%). It is suggested that the composition of the compound is best represented by the formula $Pb(O{\cdot}C_6H_5)_2,Pb(OH)(O_2C{\cdot}CH_3)$.

The compound dissolves with decomposition in warm aqueous sodium hydroxide and is not precipitated when this solution is acidified with nitric acid. It is soluble in dilute acetic acid, and this solution gives an immediate yellow precipitate with potassium chromate. It is sparingly soluble in chloroform and pure olive oil. It is also sparingly soluble in benzene, but decomposition of the compound takes place when the solution is heated.

o-*Nitrophenol compound.* A solution of *o*-nitrophenol (4 g.) in hot water was cooled to 40° and mixed with the Goulard's extract (45 c.c.), and the yellow precipitate was filtered off, washed with water (200 c.c.) at 40°, and dried in a vacuum desiccator, being obtained as a yellow, crystalline powder. When the dilute aqueous solution was allowed to stand, the substance was obtained in thin needles, which, however, were not quite pure (Found: C, 22·3, 21·5; H, 2·4, 2·0; N, 3·7; Pb, 54·6, 54·3. $C_{14}H_{12}O_9N_2Pb_2$ requires

* The lead in these compounds was conveniently determined as lead sulphate. 0·2—0·3 G. was treated with 15 c.c. of concentrated nitric acid and 10 c.c. of concentrated sulphuric acid, and the mixture evaporated almost to dryness in a beaker. The cooled residue was diluted with 20 c.c. of water and 20 c.c. of ethyl alcohol and allowed to stand for 12 hours. The lead sulphate was weighed in the usual manner. The method was checked by using pure lead acetate.

C, 21·9; H, 1·4; N, 3·7; Pb, 54·05%). It is suggested that the compound should be represented by the formula

$$Pb(O{\cdot}C_6H_4{\cdot}NO_2)_2,Pb(OH)(O_2C{\cdot}CH_3).$$

The compound explodes on heating, leaving a deposit of lead. If warmed gently, it changes in colour from yellow to red at 120—130°. As in the similar case of mercuric iodide, the reverse colour change can be brought about by rubbing. The compound dissolves in warm sodium hydroxide solution with decomposition, and nitric acid does not give any precipitate with this solution. Potassium chromate gives an immediate yellow precipitate with the solution in dilute acetic acid. The substance is slightly soluble in water, chloroform, and benzene.

o-*Bromophenol compound.* This was prepared by mixing a solution of o-bromophenol (4 g.) in water (600 c.c.) at 35° with Goulard's extract (40 c.c.). The white precipitate was washed with distilled water (200 c.c.) at 35° and dried in a vacuum desiccator over sulphuric acid (Found: C, 20·65, 20·3; H, 1·35, 1·3; Br, 21·9, 22·1, 21·7, 21·7; * Pb, 49·65, 49·6. $C_{14}H_{12}O_5Br_2Pb_2$ requires C, 20·1; H, 1·4; Br, 19·2; Pb, 49·6%). It is suggested that the compound is best represented by the formula

$$Pb(O{\cdot}C_6H_4Br)_2,Pb(OH)(O_2C{\cdot}CH_3).$$

On being heated, the substance begins to melt at 255° and later chars. It is soluble in warm sodium hydroxide solution and decomposes, nitric acid producing no precipitate and sulphuric acid giving a precipitate of lead sulphate. The substance is readily soluble in dilute acetic acid at the ordinary temperature, and addition of potassium chromate to this solution produces an immediate yellow precipitate. The substance is slightly soluble in chloroform, ethyl alcohol, and pure olive oil. It dissolves slightly in benzene, but with obvious decomposition.

The expense of this investigation is being met out of a grant from the Government Grant Committee of the Royal Society, for which we express our grateful thanks.

* In view of the constancy of the results of these bromine determinations by Carius's method made on different specimens, it is difficult to explain why they are so much higher than the suggested theoretical value, since it is highly probable that all the lead compounds described are of the same type. It is, however, significant that the redistilled o-bromophenol had a bromine content of 45·7%, but when it was mixed with pure lead acetate the apparent bromine content was 47·4%, both determinations being done simultaneously and by Carius's method (theory requires Br, 46·2%).

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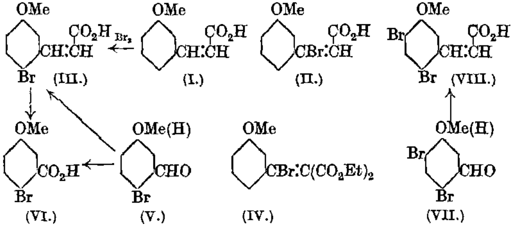
LXXX.—*The Bromination of* m-*Methoxycinnamic Acid.*

By Herbert Davies and William Davies.

Bauer and Vogel (*J. pr. Chem.*, 1913, **88**, 341) found that *m*-methoxycinnamic acid (I), when treated with one molecular proportion of bromine in glacial acetic acid, gave a substance, m. p. 186°, to which they attributed the constitution (II), since on oxidation it gave *m*-methoxybenzoic acid. They did not specify the temperature of bromination, but we have found that the bromination is effected slowly in acetic acid at the ordinary temperature, and that the acid produced, m. p. 189°, is 6-*bromo*-3-*methoxycinnamic acid* (III), its constitution being established as shown. The 6-position of the bromine atom in the bromination product (V) of *m*-methoxy (or *m*-hydroxy)-benzaldehyde has been proved by Pschorr (*Annalen*, 1912, **391**, 23). The cinnamic acid (III) prepared from this 6-bromo-3-methoxybenzaldehyde melted at 189° and was identical with the one mentioned above.

Bauer and Vogel gave no evidence for the formula (IV) which they attributed to the bromination product of ethyl *m*-methoxybenzylidenemalonate (*loc. cit.*). After hydrolysis, elimination of carbon dioxide, and oxidation, the acid obtained from this product is 6-bromo-3-methoxybenzoic acid (VI). It is possible that the bromination product of *m*-methoxybenzylidenemalonic acid also has the bromine in the 6-position, and not in the side chain as Bauer and Vogel state.

By the action of two molecules of bromine upon *m*-methoxycinnamic acid in glacial acetic acid solution, Bauer and Vogel (*loc. cit.*, p. 341) obtained a substance which they regarded as



β : 6-dibromo-3-methoxycinnamic acid (formula as II), because it could be converted into 6-bromo-3-methoxybenzoic acid. Actually,

however, the bromination product is a complex mixture, from which, after oxidation, 4(or 2) : 6-dibromo-3-methoxybenzoic acid (m. p. 203°) can be isolated, identical with the acid produced by oxidation of the 4(or 2) : 6-dibromo-3-methoxybenzaldehyde (VII) obtained from 6-bromo-3-hydroxybenzaldehyde (Hodgson and Beard, J., 1925, **127**, 877). The second bromine atom entering the nucleus may be in position 2 or 4 (compare Hodgson and Beard, J., 1926, 148, who state that the direct chlorination of *m*-hydroxybenzaldehyde gives chiefly the 2- and not the 6- or the 4-chloro-derivative).

4(or 2) : 6-Dibromo-3-methoxybenzaldebyde was converted into 4(or 2) : 6-*dibromo*-3-*methoxycinnamic acid* (VIII), m. p. 234°, and this into the corresponding benzoic acid, m. p. 203°, on oxidation.

Bromination of *m*-methoxycinnamic acid with one molecular proportion of bromine therefore gives the 6-bromo-derivative in large amount, and with two molecular proportions of bromine, two bromine atoms, to some extent, enter the nucleus. These reactions are abnormal, for bromination of cinnamic acids usually affects the double bond in the side chain, producing dibromides (Manchot, *Annalen*, 1912, **387**, 257).

EXPERIMENTAL.

m-Methoxycinnamic acid (m. p. 117°) is best prepared from the corresponding aldehyde by the action of malonic acid in pyridine, and not by the Perkin reaction, which even after prolonged treatment gives a very poor yield.

Bromination of m-*Methoxycinnamic Acid*.—The acid (10 g.) was brominated (1 mol. of bromine) in glacial acetic acid (200 c.c.) according to the directions of Bauer and Vogel (*loc. cit.*). After 2 days, much practically pure crystalline matter was collected and in the following 8 days a further quantity of less pure material separated. By crystallisation from benzene, colourless needles (4 g.), m. p. 189°, of 6-*bromo*-3-*methoxycinnamic acid* (III) were obtained (Found: C, 46·8; H, 3·5. $C_{10}H_9O_3Br$ requires C, 46·7; H, 3·6%). It is oxidised by permanganate (without the production of potassium bromide) to give 6-bromo-3-methoxybenzoic acid (m. p. 162°) (VI). 6-Bromo-3-methoxycinnamic acid was also synthesised from 6-bromo-3-methoxybenzaldehyde (m. p. 76°, prepared after Pschorr and also Hodgson and Beard, J., 1925, **127**, 877) by means of malonic acid in pyridine.

After the brominating liquor had stood for 10 days, it was diluted with water, and gave a solid, m. p. 108—140°, from which nothing pure could be crystallised; but it undoubtedly contained a cinnamic acid dibromide derivative, because, when it was warmed with

sodium acetate, bromide was produced together with an oily, styrene-like substance.

Bromination of m-*Methoxybenzylidenemalonate.*—This substance, b. p. 205—208°/17 mm., prepared after Bauer and Vogel, was heated on the water-bath with bromine (1 mol.) in 100% acetic acid for 3 hours; bromination was then complete. The product obtained on pouring the mixture into water was hydrolysed with sodium hydroxide, and the acid (m. p. 173—183°, decomp.) obtained on acidification was dried and heated at 180° until the evolution of carbon dioxide ceased. The product, after crystallisation from benzene, melted at 189° before and after admixture with 6-bromo-3-methoxycinnamic acid. They were also found identical in other respects.

The Action of Two Molecules of Bromine on m-*Methoxycinnamic Acid.*—*m*-Methoxycinnamic acid (10 g.) was heated on the water-bath with bromine (2 mols.) after Bauer and Vogel, who record no temperature; bromination was complete in 8 hours. The product obtained on pouring the mixture into water separated from dilute acetic acid (without the application of heat) in colourless crystals, m. p. 130—163°. This substance at once reduced permanganate in cold acetone, and when it was treated with cold alkali or sodium acetate an oil of styrene-like character and a bromide were formed. The bromine was evidently partly in the side chain. The acid (m. p. 130—163°), after being ozonised in dilute acetic acid solution at the ordinary temperature, melted at 157—165° and contained Br, 52·8% (Calc. for 3Br, 57·5; for 2Br, 47·3%). The product, on oxidation with permanganate, gave a small quantity of 4(or 2) : 6-dibromo-3-methoxybenzoic acid, m. p. 203°, which was identified by the method of mixed melting point.

Monobromination of 6-bromo-3-methoxycinnamic acid produced the mixed acids, m. p. 157—165°. Bromination therefore takes place partly at the double bond in the side chain and partly in the nucleus.

4(or 2) : 6-*Dibromo-3-methoxycinnamic acid* (VIII) was synthesised for purposes of comparison. 4(or 2) : 6-Dibromo-3-hydroxybenzaldehyde (m. p. 139°) was prepared after Hodgson and Beard (*loc. cit.*), but instead of isolating the monobromo-derivatives of 3-hydroxybenzaldehyde it was found advantageous to heat the aldehyde with one mol. of bromine in chloroform and, when that had reacted, to add the second mol. of bromine. Subsequent methylation and steam distillation gave 4(or 2) : 6-dibromo-3-methoxybenzaldehyde, m. p. 110° as found by Hodgson and Beard. This was converted into the corresponding cinnamic acid exactly as in the preparation of 6-bromo-3-methoxycinnamic acid. 4(or 2) : 6-*Dibromo-3-methoxycinnamic acid* separates from acetic acid

colourless prisms, m. p. 234° (Found : equiv., 334·7. $C_{10}H_8O_3Br_2$ requires equiv., 336). It decolorises permanganate in cold acetone solution and is oxidised, without the formation of bromide, to give 4(or 2) : 6-dibromo-3-methoxybenzoic acid, m. p. 203°.

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LXXXI.—*The Alkaline Hydrolysis of ω-Bromo- and ω-Chloro-nitrostyrenes.*

By ARTHUR THURLBY DANN, ALF HOWARD, and WILLIAM DAVIES.

THERE appears to be in the literature no definite statement that the influence of a group may be transmitted through a mixed aliphatic aromatic conjugated system, as it undoubtedly is through certain conjugated purely aromatic or aliphatic compounds. Some evidence of the effect of ω-substituents in styrene derivatives is available as far as nitration is concerned. Both cinnamic acid and ω-nitrostyrene (Priebs, *Annalen*, 1884, **225**, 347) give negligible quantities of meta- in comparison with ortho-para-substitution products, and Flürscheim (*J. pr. Chem.*, 1902, **66**, 19) has shown that ω-bromostyrene yields *p*- and *o*-nitro-derivatives. These instances contrast with the nitration of α-nitro-β-phenylethane (Holleman and de Bruyn, *Rec. trav. chim.*, 1900, **19**, 79) and of salts of β-phenylethylamine (Goss, Hanhart, and Ingold, J., 1927, 250), in which about 13% of the *m*-nitro-derivative is produced. It is difficult to believe that a saturated aliphatic chain can transmit the effect of a group already present better than an unsaturated conjugated chain.

The problem of the transmission of the influence of one group in a styrene throughout the molecule has been attacked from the reverse point of view, namely, by comparing the activating effects of the nitro-group in different positions in the nucleus on the ω-halogen atom in the *trans-o-*, *m-*, and *p*-nitro-ω-halogenostyrenes.

The reaction involved was that of aqueous-alcoholic potassium hydroxide and the halogenonitrostyrenes at different temperatures, the amounts of potassium bromide (or chloride) produced when the isomerides were subjected to identical and simultaneous treatment being compared. Probably some other reaction than the two already mentioned occurs, as the ω-halogeno-*p*-nitrostyrenes give an intense red colour with alcoholic potassium hydroxide in the cold.

Nef (*Annalen*, 1899, **308**, 268) has shown that the action at 130—135° of alcoholic potassium hydroxide on ω-bromostyrene is to give phenylacetylene and β-ethoxy-α-phenylethylene. These

reactions, although quite distinct, are both due to the mobility of the bromine atom.

In the higher-melting bromonitrostyrenes (which have been called the *trans*-forms), the reactivity of the bromine atom is in the order ortho>para>meta. The order for the chloro-analogues is similar, being para>ortho>meta. It is thus seen that the nitro-group has a greater effect when it is in the ortho- or para-position than when it is in the meta-position, and it follows that its effect is transmitted through the side chain in apparently the same way as it is through the benzene nucleus. Otherwise it is difficult to explain why the nitro-group should have a greater activating influence in the para-position than in the meta-position, in which (if the usual formulæ for benzene are adopted) it is nearer the halogen atom.

This research, however, has brought to light two unexpected facts which must be taken into consideration. The first is that the *cis*- and *trans*-ω-bromo-*p*-nitrostyrenes have a difference of activity of the order of that separating the *trans*-*m*- and *trans*-*p*-compounds. The unsubstituted *cis*- and *trans*-ω-bromostyrenes also present marked differences in activity. Now since ω-bromo-*p*-nitrostyrene is only about 1·25 times as much attacked by the alkali as the *m*-nitro-isomeride (when a total conversion of between 3 and 4% has been brought about; see Table I), it is possible that the great difference in activity of the geometrical isomerides of the same substance may, if the *cis*- changes into the *trans*-form during the reaction, prevent the results obtained being true criteria of the effects of the differently situated nitro-groups. Although possible, this is not probable because the unsubstituted *cis*- and the *cis*-*p*-nitro-ω-bromostyrenes, which are more reactive than the *trans*-forms, only show a tendency to change into the geometrical antimerides in bright light.

cis-ω-Chloro-*m*-nitrostyrene has not been isolated in a pure condition, nor its reactivity investigated. *trans*-ω-Chloro-*m*-nitrostyrene is more reactive at low and less reactive at high temperatures than ω-chlorostyrene (doubtless a mixture of the *cis*- and *trans*-forms) (see Table II and the discussion of results). This phenomenon may be due to the more reactive, geometrically isomeric ω-chlorostyrene being produced at high temperatures, whereas the *trans*-*m*-nitro-derivative may remain in the *trans*-form. In any event, the surprisingly great difference in reactivity of the geometrical isomerides of the same substance encourages the seeking of other and more cogent evidence of the transmission of group influences through a styrene molecule.

Light has been of great assistance in changing *cis*-ω-bromo-*p* nitrostyrene into the otherwise less accessible *trans*-form.

EXPERIMENTAL.

Nitro-ω-bromostyrenes.—The three nitrocinnamic acids (these are best obtained, the *o*- and *m*-compounds from the nitrobenzaldehydes by the Perkin reaction, and the *p*-compound from ethyl cinnamate by nitration and subsequent hydrolysis), when made into a thin paste with glacial acetic acid and treated at 100° with bromine (1 mol.), were converted within a few hours almost quantitatively * into the αβ-dibromo-β-nitrophenylpropionic acids. These were heated in 30% aqueous sodium acetate (5 mols.) for 4—6 hours and the nitro-ω-bromostyrenes were then isolated by distillation in steam. Each of these was separated by distillation in a vacuum into a high-boiling (which solidified almost completely) and a low-boiling form. The latter in ethereal or benzene solution, when exposed in a silica vessel to sunlight or the ultra-violet light from a 1000-watt mercury lamp, was largely converted into the high-melting form, which was obtained pure by crystallisation from alcohol. When exposed in the solid state to light, these bromonitrostyrenes acquire a much deeper yellow colour. They all have pleasant odours.

The ω-*bromo*-o-*nitrostyrenes* (yield, about 20%). The *cis*-form (collected up to 165°/21 mm.) does not solidify at 0°. The *trans*-form boils at 165—167°/21 mm. and separates from alcohol in light yellow prisms, m. p. 39° (Reich and Chang, *Helv. Chim. Acta*, 1920, **3**, 240, record m. p. 70°; which is possibly a misprint for 40°) (Found: Br, 35·2. Calc.: Br, 35·1%).

The ω-*bromo*-m-*nitrostyrenes* (yield, about 35%). The solid form boils at 150°/18 mm. and separates from alcohol in very light yellow needles, m. p. 77° (Wollring, *Ber.*, 1914, **47**, 110, records m. p. 78—79°: Reich and Koehler, *Ber.*, 1913, **46**, 3733, give m. p. 59°). The *cis*-form suffers only a slight conversion into the high-melting form through the action of light.

The ω-*bromo*-p-*nitrostyrenes* (yield, more than 50%). The mixture melts at 40—60° and mostly consists of the low-melting form, contrary to the statement of Reich and Chang (*loc. cit.*, p. 239) that the use of aqueous sodium acetate gives the high-melting form. *trans*-ω-Bromo-*p*-nitrostyrene boils at 182°/21 mm. and separates from alcohol or light petroleum in minute, very pale yellow needles, m. p. 160° (Reich and Chang, *loc. cit.*, record m. p. 123°), unchanged by sublimation in a cathode ray vacuum (Found: Br, 34·8; *M*, by Rast's method, 224. Calc.: Br, 35·1%; *M*, 228).

* The difficulty in brominating these acids reported in the literature (Müller, *Annalen*, 1882, **212**, 122; Beilstein's "Handbuch," 3rd edn., II, p. 1414) was due to the selection of an unsuitable solvent.

cis-ω-Bromo-p-nitrostyrene, which cannot be obtained pure from the mixture described above, is produced unaccompanied by the *trans*-form when αβ-dibromo-β-*p*-nitrophenylpropionic acid is heated with alcoholic instead of aqueous sodium acetate (Reich and Chang, *loc. cit.*). It crystallises from light petroleum (b. p. 40—60°) in thick, yellow prisms, m. p. 49°, b. p. 168—170°/21 mm. (Found; *M*, by Rast's method, 236).

The Action of Light on cis-ω-*Bromo*-p-*nitrostyrene*.—A dilute benzene solution, 5 mm. deep, of the pure *cis*-form (m. p. 49°) was exposed in a clear silica test-tube to bright sunlight for 4 hours, and after removal of the benzene the melting point was 95—140°. Similarly, a mixture of the two forms (m. p. 40—60°) in benzene solution was converted in bulk into a mixture, m. p. 115—150°, after 30 hours' exposure to sunlight. From such a mixture the pure *trans*-form is easily obtained by crystallisation from alcohol. Photo-conversion in solutions in glass vessels is also quite rapid, and the solid *cis*-form is unstable to sunlight. When spread in thin layers, the pure *cis*-form has its melting point raised from 49° to 45—70° after 2 hours' exposure to sunlight. It had previously been noted that it was impossible to obtain the pure *cis*-form by crystallisation in bright light.

ω-*Bromostyrene*.—The two forms, m. p. −7° and +7° respectively, have been isolated by Dufraisse (*Compt. rend.*, 1920, **171**, 960), who found that exposure to light changed both forms into a mixture, m. p. 2°, containing a large proportion of the higher-melting isomeride. Our experiments, probably partly owing to different lighting conditions, gave one form, m. p. −5° to −2·5°, b. p. 105°/18 mm., and another form, m. p. 2·2°, b. p. 120°/29 mm. These mixtures must have contained relatively large amounts of the *cis*- and *trans*-forms respectively, because the lower-melting form remained almost colourless, whereas that melting at 2·2° soon became deep yellow and finally brown even in the dark. This behaviour is characteristic of the two forms isolated by Dufraisse (*loc. cit.*). The low-melting isomeride is converted into the mixture, m. p. 2·2°, by the action of light. This mixture, m. p. 2·2°, and the mixture, m. p. −5° to −2·5°, were examined from the point of view of comparative mobility of the bromine atom (see Table I).

Nitro-ω-chlorostyrenes.—Into an ice-cold solution of the nitro-cinnamic acid in sodium carbonate a slow stream of carbon dioxide is passed, and a cold solution of sodium hypochlorite is gradually added, during 8 hours. The product is then steam-distilled, the styrene derivative being obtained in the high-melting form without a trace of the low-melting isomeride (yield, 5—15%). All these chloronitrostyrenes have pleasant odours.

ω-Chloro-*o*-nitrostyrene forms very pale yellow needles, m. p. 58° (Lipp, *Ber.*, 1884, **17**, 1070, records m. p. 58—59°). *ω-Chloro*-m-*nitrostyrene* crystallises from alcohol in short, thick, yellow prisms, m. p. 83° (Found: Cl, 19·4. $C_8H_6O_2NCl$ requires Cl, 19·4%), which rapidly deepen in colour on exposure to light. *ω-Chloro*-p-*nitrostyrene* crystallises from alcohol, in which it is much less soluble than the two preceding isomerides, in very pale yellow, minute needles, m. p. 128° (Found: Cl, 19·4%).

ω-Chlorostyrene is best prepared by taking advantage of the formation of αβ-dichloro-β-phenylpropionyl chloride by the interaction of cinnamic acid and phosphorus pentachloride (Clarke, J., 1910, **97**, 894). The acid chloride was isolated, the acid decomposed with sodium acetate, and the styrene fractionated, a colourless oil, b. p. 92—93°/22 mm., which slowly became pale yellow, being obtained (yield, 60%).

TABLE I.

Hydrolysis of the ω-Bromostyrenes.

Bromostyrene.	Experiment. Temp. Time (hours). I. 14°. 24.	II. 17°. 18.	III. 17—24°. 117·5.	IV. 41—41·3°. 16.	V. 39·3—41·3°. 5.	VI. 40·7—42·0°. 16.
	Percentage conversion.					
o-Nitro-	99·5	99·5	—	—	—	—
m- ,, ...	3·30	3·82	4·69	—	—	—
p- ,, , m. p. 160° ...	4·15	4·45	30·8	48·8	18·7	—
Unsubs., m. p. 2·2° ...	—	4·37	11·3	12·41	—	13·9
,, m. p. −2·5°	—	—	15·07	17·9	—	18·74
p-Nitro-, m. p. 49°	—	—	—	98·51	98·1	—

Procedure.—The bromostyrene (0·001—0·002 g.-mol.) was dissolved in cold alcohol and after the correct temperature had been attained, 5·0 c.c. of 7*N*-potassium hydroxide were added. The product was worked up on a macro-scale as described for the chloro-compounds. The amount of alcohol (98·6%) required to dissolve 0·002 g.-mol. of ω-bromo-*p*-nitrostyrene was about 180 c.c. The comparisons were made under identical conditions of concentration and temperature, and were carried out simultaneously. The results recorded in Table I are discussed after Table II.

TABLE II.

Hydrolysis of the ω-Chlorostyrenes.

Chlorostyrene.	Experiment. Temp. Time. I. 40·3—41·3°. 20 hrs.	II. 41—41·3°. 20 hrs.	III. 81°. 125 mins.	IV. 81°. 125 mins.
	Percentage conversion.			
Unsubs.	5·65	5·7	37·95	36·3
o-Nitro-	33·6	34·3	101·4	100·2
m- ,, ...	11·7	12·1	23·6	24·2
p- ,, ...	64·9	68·0	100·7	100·5

Procedure.—0·001 G.-mol. (0·1835 g. of the chloronitrostyrene; 0·1385 g. of ω-chlorostyrene) was made up to 100 c.c. in alcohol. 10 C.c. of this solution were treated with 10 c.c. of alcohol and 10 c.c. of 2*N*-potassium hydroxide. The comparison of the four substances in each experiment was made at the same time, either in a thermostat or at the boiling point (81°). After the reaction had finished, the product was washed out by water and a little alcohol into a large boiling-tube, nitric acid and silver nitrate were added, and the silver chloride was coagulated by heating the mixture nearly to the boiling point in a beaker of water. By having the level of the water in the beaker above that of the solution in the tube and by keeping the temperature below that of boiling water, the sudden disastrous evolution of acetaldehyde, generated by the action of nitric acid on the alcohol, was prevented. The silver chloride was estimated after Pregl. It is advisable, before drying, to wash the filter tube with hot alcohol to remove traces of precipitated styrene. This is particularly necessary when working with the very sparingly soluble ω-chloro-*p*-nitrostyrene. The alcohol used throughout these micro-experiments was methylated spirit, consisting of ethyl alcohol (91·6%), water (6·4%), and methyl alcohol (2%).

The experiments were carried out in the dark or in diffused daylight. The chlorostyrenes are too non-reactive at the ordinary temperature for the decomposition to be measurable. Even at the ordinary temperature, however, the solution containing the para-compound became red on standing. On boiling, the ortho-compound gave a very pale yellow solution, but the unsubstituted and the *m*-nitro-chlorostyrene remained colourless.

Discussion of the Results.—From the results in Table I for the *trans*-ω-bromostyrenes it is seen that (1) the *o*-nitro-compound is extraordinarily reactive, (2) at the temperatures investigated, the *p*- is more reactive than the *m*-nitro-compound; the ratios of the conversion in experiments (I) and (II), in which only a small percentage conversion was obtained, are respectively 1·26 and 1·23 to I, (3) the order of activity of the bromine atom is ortho>para>unsubstituted>meta. It must be remembered, however, that the unsubstituted bromostyrene (m. p. 2·2°) contained some of the more reactive *cis*-form.

The *cis*-*p*-nitro- is far more reactive than the *trans*-*p*-nitro-compound (see experiments IV and V), and the unsubstituted bromostyrene (m. p. −2·5°), which contains much of the *cis*-form, is more reactive than the mixture, m. p. 2·2°, which is richer in the *trans*-form (experiments IV and VI).

For the ω-chlorostyrenes (Table II) the order of activity of the halogen atom is, at about 41°, para>ortho>meta>unsubstituted,

and at 81°, (para and ortho)>unsubstituted>meta. An explanation of the inversion of the order for the *m*-nitro- and the unsubstituted ω-chlorostyrene is suggested on p. 606. It is also possible that two reactions occur simultaneously between the alkali and the nitro- and the unsubstituted styrene. A similar phenomenon is noticeable, though to a less extent, in the *m*- and *p*-nitro-ω-bromostyrenes (see experiments I, II, and III in Table I), where increase in temperature from 17° to 17—24° increases the activity of the *p*- far more than that of the *m*-isomeride.

The authors wish to thank Mr. G. W. Leeper, M.Sc., for assistance in the initial stages of this work.

MELBOURNE UNIVERSITY. [*Received, November 21st,* 1927.]

LXXXII.—*Derivatives of γ-Xylose. A Study of Xylosemonoacetone and its Conversion into 2:3:5-Trimethyl γ-Xylonolactone.*

By WALTER NORMAN HAWORTH and CHARLES RAYMOND PORTER.

THE lactones related to simple methylated sugars may be prepared (*a*) by direct oxidation of the methylated sugar itself or alternatively (*b*) by methylation of the lactone derived from the unsubstituted sugar by oxidation. The latter method possesses the disadvantage that during conversion of the unmethylated lactone into the methylated lactone the former may change its identity by the opening of its ring and subsequent closure to give an isomeric lactone. Certain δ-lactones pass with remarkable ease under a variety of conditions to the more stable γ-lactones (unsubstituted). It is obvious also that where the methylation of a lactone is accompanied by scission involving the formation of an ester, structural considerations rest on a precarious basis if it be assumed that the ester, on hydrolysis, necessarily passes to the same structural type of lactone as the original unmethylated one.

The first method of preparing the methylated lactones (method *a* above) is the more satisfactory, and especially so, fortunately, for the δ-lactones which are obtained with some difficulty by method (*b*). Since the purity of the lactone is dependent, however, on the homogeneity of the methylated sugar, and since there has hitherto been no satisfactory standard of purity for the γ-sugars, which may, and probably do in some cases, contain some of the methylated normal sugar, the purity of the lactones prepared by oxidation of the γ-sugars may be under suspicion. This criticism does not

apply to those γ-lactones which have been obtained in a crystalline condition, and it is thus restricted to the two known cases of the liquid trimethyl γ-xylonolactone and tetramethyl γ-galactonolactone, for which special reservations were made in the provisional data given in the earlier communication (Drew, Goodyear, and Haworth, J., 1927, 1237).

The study of the so-called γ-sugars (furanoses) is being pursued with the object of obtaining in every case structurally, and also optically, pure specimens. An obvious procedure to this end is to prepare them from homogeneous specimens of γ-lactones. In the present paper, the isolation of the highly pure trimethyl γ-xylonolactone is communicated, the procedure being that of a combination of methods (*a*) and (*b*). The satisfactory evidence of purity rests on the formation of the crystalline phenylhydrazide derivative, followed by regeneration therefrom of the lactone.

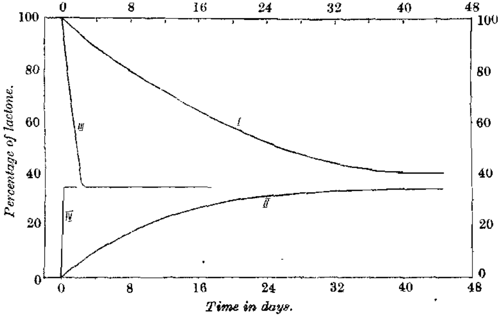
The crystalline xylose-monoacetone described by Svanberg (*Ber.*, 1923, **56**, 863, 2195) gave on methylation with methyl sulphate and alkali a dimethyl xylose-monoacetone, $[\alpha]_{5790}^{15^\circ}$ − **46·6°**. Hydrolysis of the latter, followed by oxidation of the liberated dimethyl xylose, yielded a dimethyl γ-xylonolactone having $[\alpha]_{5780}^{21 \cdot 5^\circ}$ + 81·5°, changing slowly in aqueous solution to + 39° after 49 days. The crystalline phenylhydrazide (m. p. 94—95°) of the corresponding acid was prepared. Further methylation of the lactone yielded the trimethyl γ-xylonolactone, which gave a crystalline phenylhydrazide, m. p. 89—90° (yield 75%). This phenylhydrazide was also obtained from the specimen of the trimethyl γ-xylonolactone isolated by Haworth and Westgarth (*J.*, 1926, 880) by oxidation of trimethyl γ-xylose. The constitution of the latter sugar was given by those authors as a butylene oxide (xylofuranose), and that conclusion is verified by the following experimental results. From the crystalline phenylhydrazide the purified lactone was regenerated and this was submitted to polarimetric study and its constitution was also determined by oxidation methods. The rate of conversion of the trimethyl γ-xylonolactone in aqueous solution into the corresponding trimethyl xylonic acid and also the reverse change from the acid to the lactone were calculated from the rotation figures recorded in the experimental section. The percentage of acid present in aqueous solution at any given time during the hydrolysis of the lactone is calculated from the expression $100(R - R_l)/(R_a - R_l)$ which has previously been used (Drew, Goodyear, and Haworth, *loc. cit.*; compare evene and Simms, *J. Biol. Chem.*, 1925, **65**, 46): R is the specific tion of the solution at a given time and R_a and R_l are the halo rotations of the lactone in the form of acid and of the

lactone respectively. It has been explained in the earlier paper (*v. supra*) that the values determined on this experimental basis are probably not strictly accurate, but they are considered sufficiently exact to be applicable to the present purpose the authors have in view, namely, to furnish a preliminary groundwork for the study of the conditions influencing the markedly different rates of hydrolysis of γ- and δ-lactones related to simple sugars.

In Fig. 1 are given the curves illustrating the percentage lactone present at any given time during the conversion of (I) trimethyl γ-lactone into the acid, and (II) the acid into the lactone. For the sake of comparison with the trimethyl δ-xylonolactone the

FIG. 1.

Comparative rates of hydrolysis of the isomeric trimethyl xylonolactones and the rates of the reverse change of acids into lactones.



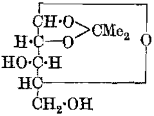
curves III and IV are also included from the previous paper by Drew, Goodyear, and Haworth.

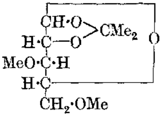
The time period during which the equilibrium γ-lactone ⇌ γ-hydroxy-acid is attained must obviously be greater than 900 hours. As in previous cases the time required for the development of 25% of the xylonic acid may be more accurately ascertained, and this is seen to be 250 hours instead of the approximation of 430 hours previously suggested (Drew, Goodyear, and Haworth, *loc. cit.*). This time period is to be contrasted with the corresponding period for the isomeric δ-lactone, which is 22 hours. Equilibrium is attained very rapidly from the side δ-hydroxy-acid to δ-xylonolactone and the steepness of curve IV suggests that the reaction is being promoted either by catalysis by the organic acid itself or

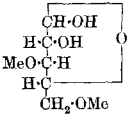
by the presence of the mineral salt (sodium sulphate) which is unavoidable under the experimental method adopted. The latter effect is much less marked in curve II.

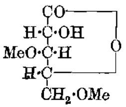
Finally, the constitution of the 2 : 3 : 5-trimethyl γ-lactone was confirmed by its oxidation to *d*-dimethoxysuccinic acid (VI), which was recognised through the crystalline methylamide, m. p. 204—205°. The latter was identical with a specimen specially prepared for this comparison by Haworth and Jones (J., 1927, 2349) from *d*-tartaric acid.

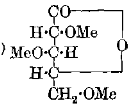
Interpretation of the experimental evidence furnished by these results leads definitely to the conclusion that the dimethyl xylonolactone (IV) employed as a source of the trimethyl γ-xylonolactone (V) was also itself a γ-lactone. Inasmuch as the dimethyl lactone (IV) originated from a dimethyl xylose, it follows that the latter was a butylene oxide or γ-sugar, that is, a xylofuranose (III), which was obtained by the hydrolysis of (II). From this it is also argued that the non-reducing xylose-monoacetone also contained a butylene-oxide ring, formulated as in (I).

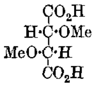

(I.)

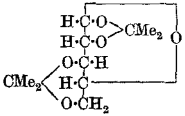

(II.)

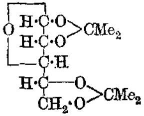

(III.)

(IV.)


(V.)



(VI.)

(VII.)


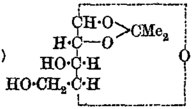

(VIII.)

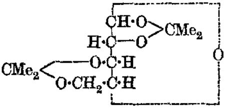
It must be conceded that no alternative interpretation of the structure of xylose-monoacetone (I) is possible in view of these experimental results. The oxide ring in this γ-sugar derivative is stabilised as effectively as in the case of γ-methylglucoside. Whether the same oxide ring structure applies also to xylose-diacetone as shown in (VII) is a case for further argument. Origin-

illy we had hoped that the present experiments would yield evidence n favour of the formula (VIII), since this presented a unique pportunity to investigate the possible existence of 1 : 3 or propylene-xide sugars which are at present unknown, although their existence ias frequently been postulated. The formula (VIII) represents he two acetone residues as connecting *cis*-hydroxyl groups attached o contiguous carbon atoms, a condition which seems to be fulfilled n all other authentic structural formulæ for sugar-acetones.

On the other hand, if xylose-diacetone exists according to the tructural scheme (VIII), then the 1 : 3-oxide ring has undergone a lisplacement to the 1 : 4-oxide simultaneously with the removal of ne acetone residue to form the monoacetone (I). This is indeed , possibility, but a careful review of the whole of the evidence leads is *to the alternative decision in favour of the formulation* (VII) or xylose-diacetone.

Inspection of the atom-models arranged either to represent VII) or (VIII) indicates a marked preference for (VII) on the rounds of minimum internal strain. One of us has already directed ttention to the failure of plane formulæ to represent the spatial elationship of groups at the ring-forming carbon atom intermediately ituated in the chain (Drew and Haworth, J., 1926, 2303). When hese are correctly represented in xylose-monoacetone and the xygen of the oxide ring is shown to be co-planar with the first our carbon atoms of the sugar chain, it is seen (formula IX) that he 5th carbon atom of the chain is directed to the left in proximity o the hydroxyl at the 3rd carbon atom and this pair of hydroxyl roups is favourably placed to receive an acetone residue thus formula X):

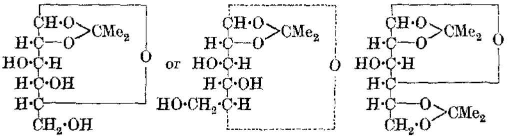
IX.) 

 (X.)

n these circumstances the internal strain is minimised and is omparable in magnitude with that associated with the union of n acetone group with *cis*-hydroxyl groups at contiguous carbon toms.

If the hydroxyl at the third carbon atom had been directed to he right instead of to the left, this type of six-ring formation with cetone could not have occurred except under exceptional strain. dopting the conventional plane formula for oxide rings in sugars, t may be laid down as a suitable rule that where the above type f *condensation with acetone is favoured the hydroxyl at a carbon*

within the oxide ring of the sugar must not be on the same side as the oxide ring. It is probably for this reason that glucose does not condense with acetone while existing as a pyranose, or an amylene-oxide form, since inspection of formula (XI) shows that the hydroxyl at the fourth carbon is to the right of the formula and so also is the oxide ring.



(XI.) (XII.)

The formulation of glucose-diacetone on the plan of Levene, Freudenberg, and Karrer as a butylene-oxide sugar derivative or a furanose is the only scheme which leads to minimum strain in the models (formula XII). There is just as much experimental evidence for the formulation (VII) for xylose-diacetone as there is for the formulation (XII) of glucose-diacetone.

EXPERIMENTAL.

Methylation of Xylose-monoacetone.—Xylose-diacetone (13·43 g.) was dissolved in 300 c.c. of 0·2% hydrochloric acid at 17° and the hydrolysis was followed by taking polarimetric readings in a 2-dcm. tube. The rotation was α + 0·56° (after 10 mins.), falling to a constant value, α − 1·28° (after 100 mins.). The solution was neutralised with barium carbonate, filtered, evaporated at 35° and gave xylose-monoacetone (Svanberg, *loc. cit.*). The substance was now methylated with methyl sulphate and sodium hydroxide in the usual way, first at 35—45° and finally at 60—70°. The product was extracted with chloroform, again methylated, and distilled, b. p. 75—78°/0·07 mm. (yield, 10 g.). The dimethyl xylose-monoacetone showed $[\alpha]_{5780}^{15^\circ}$ − 46·6°; $n_D^{15^\circ}$ 1·4455.

Dimethyl γ-Xylonolactone.—This was prepared by the combined hydrolysis and oxidation of dimethyl xylose-monoacetone. The latter (5·6 g.) was heated at 85° with 2·7% hydrobromic acid (65 c.c.) for an hour. Bromine (6 c.c.) was then gradually admitted to the solution, which was kept at 75°. (Bromination of some of the liberated acetone occurred.) After 15 hours the solution was neutralised with lead carbonate, and treated with silver oxide followed by hydrogen sulphide in the usual way, and the organic acid was isolated as the lactone, which distilled at 105—106°/0·06

mm. Yield, 3·55 g. of distilled lactone. The dimethyl xylonolactone showed $n_D^{15°}$ 1·4643; $[\alpha]_{5780}^{21.5°}$ + 81·5° (after 3 mins.), 85·1° (after 1 day), 83·2° (2 days), 66·9° (7 days), 54·5° (14 days), 44·1° (21 days), 39·6° (40 days), 39° (49 days) (Found : C, 47·1; H, 6·9; OMe, 32·7. $C_7H_{12}O_5$ requires C, 47·7; H, 6·8; OMe, 35·2%).

Phenylhydrazide. The dimethyl γ-xylonolactone and phenylhydrazine in molecular proportion were mixed in dry ether, the solvent was evaporated, the mixture heated during an hour on the water-bath and cooled, and the solid product triturated with ether and finally recrystallised from benzene. It was obtained as rosettes of needles, m. p. 94—95°, soluble in chloroform, less so in ether or water, and insoluble in light petroleum (Found : C, 55·1; H, 7·1; N, 10·15; OMe, 19·5. $C_{13}H_{20}O_5N_2$ requires C, 54·9; H, 7·0; N, 9·9; OMe, 21·8%).

Phenylhydrazide of the Acid corresponding to Trimethyl γ-Xylonolactone.—The above dimethyl xylonolactone was twice methylated by Purdie's reagents, and gave a colourless liquid, b. p. 84°/0·1 mm., $n_D^{15.5°}$ 1·4472, which was the crude trimethyl γ-xylonolactone (Found : C, 50·2; H, 7·4; OMe, 49·0. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 49·0%). The *phenylhydrazide* was prepared in a similar way to that described above, and gave (75% of the theoretical yield) rosettes of needles, m. p. 89—90°, crystallised from benzene. The same substance was also prepared from a specimen of the trimethyl γ-xylonolactone prepared by Haworth and Westgarth (*loc. cit.*) from trimethyl γ-xylose, but the yield in this case was not so high (Found : C, 56·2; H, 7·3; N, 9·8; OMe, 27·7. $C_{14}H_{22}O_5N_2$ requires C, 56·4; H, 7·4; N, 9·4; OMe, 31·2%).

Regeneration of the Purified Trimethyl γ-Xylonolactone from the above Crystalline Phenylhydrazide.—The phenylhydrazide (m. p. 89—90°) of the acid corresponding to this lactone was hydrolysed with a slight excess of *N*/10-hydrochloric acid at 90°, the solution evaporated at 35° under diminished pressure, and the residue dried. The lactone obtained was dissolved in dry ether containing a little chloroform, the solution treated with charcoal, and the trimethyl xylonolactone distilled, b. p. 82°/0·06 mm.; $n_D^{17°}$ 1·4464.

The rate of hydrolysis of the lactone was studied by the polarimetric method, aqueous solutions being used. The rate of conversion of the free trimethyl xylonic acid into the lactone was similarly studied; for this purpose the lactone was hydrolysed by the addition of the equivalent amount of sodium hydroxide, and to this aqueous solution of the sodium salt the equivalent of dilute hydrochloric acid was admitted to liberate the free acid in solution. Polarimetric readings were taken immediately and over a period of 43 days.

	Conversion of lactone into acid (c = 1·998).		Conversion of acid into lactone (c = 0·856) (calc. as lactone).	
Time (days).	$[\alpha]_{5780}^{17^\circ}$.	$[\alpha]_{5461}^{17^\circ}$.	$[\alpha]_{5780}^{17^\circ}$.	$[\alpha]_{5461}^{17^\circ}$.
0	+108°	+118°	+42·5°	+46°
1	110	120	40	45·5
2	108	117	40	42·5
7	98	108	49	52
9	95·5	104·5	52	55·5
14	88·5	96	55	58·5
19	81·5	88·5	58	61·5
26	75	80	62	66
29	73	78·5	61·5	66
33	70	75·5	62	68
40	67·5	73	62·5	67
43	67·5	72·5	62·5	68

Oxidation of Trimethyl γ-Xylonolactone.—The above lactone was oxidised by heating at 95—100° for 8 hours with nitric acid (d 1·42). The cooled solution was diluted with water and evaporated under diminished pressure during successive additions of water. This treatment was followed by the repeated addition of methyl alcohol and evaporation of this solvent. The syrupy residue was esterified by digestion with methyl-alcoholic hydrogen chloride (3%), and the ester isolated by neutralisation with silver carbonate, filtration, evaporation, and extraction with ether. The residue remaining after evaporation of the ether was distilled under 0·15 mm. from a bath heated at 117—120°. The colourless distillate showed $n_D^{14^\circ}$ 1·4429, and amounted to rather more than one-fourth of the weight of the original lactone. It appeared to be the methyl ester of a dibasic methoxy-acid, and was characterised by the following experiment.

The ester was dissolved in dry methyl alcohol, cooled in ice and saturated with dry methylamine. After being kept for a day, the solution was evaporated in a vacuum and yielded a crystalline product which, purified from ethyl acetate, had m. p. 204—205°. A mixture of the crystals with an authentic specimen of d-dimethoxysuccinomethylamide prepared from d-tartaric acid (Haworth and Jones, *loc. cit.*) showed no depression. There can therefore be no doubt that the trimethyl γ-xylonolactone yielded on oxidation as the only product recognisable by these methods, d-dimethoxysuccinic acid.

The authors are indebted to the Chemical Society for a grant towards the purchase of the materials used in this research.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, January 10th, 1928.*]

LXXXIII.—*Polysaccharides. Part I. The Structure of Inulin.*

By Walter Norman Haworth and Abraham Learner.

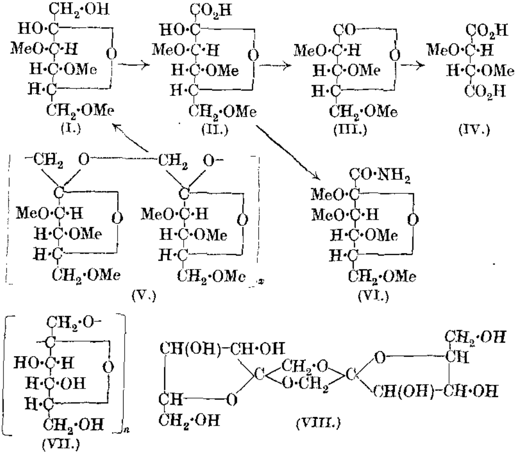
Experimental methods which we have found serviceable in the elucidation of the structure of the fructose component in sucrose have now been applied to the problem of the structure of inulin. From the results now communicated, a knowledge has been gained of the hydroxyl positions through which the fructose residues are linked to each other in inulin. Although this polysaccharide has been studied by previous workers and methylated to give trimethyl inulin (Irvine and Steele, J., 1920, **117**, 1474; Irvine, Steele, and Shannon, J., 1922, **121**, 1060; Karrer, *Helv. Chim. Acta*, 1921, **4**, 253) and the polysaccharide has been described as a complex of condensed γ-fructose residues, yet the characterisation of the trimethyl γ-fructose obtained from this source has not hitherto been achieved.

Inulin responded readily to methylation by means of methyl sulphate and sodium hydroxide, and, as in the case of sucrose (Haworth, J., 1915, **107**, 8), one treatment with these reagents yielded a product which was completely soluble in methyl iodide; thereafter the methylation was completed by the use of Purdie's reagents. These operations did not lead to the formation of dextrorotatory by-products as described by Irvine and his co-workers (*loc. cit.*), but gave an apparently homogeneous trimethyl inulin which separated as a white, amorphous powder. Under the present conditions it has not been found possible to avoid the use of considerable concentrations of alkali in the first methylation process, and the results now communicated are subject to the assumption that no fundamental change has occurred in the character or mode of linking of the polysaccharide due to this treatment with alkali. We have been able to detect no apparent change in the nature of inulin after subjection to this alkaline treatment. Alkali hydroxide compounds of inulin are indeed described (Pfeiffer and Tollens, *Annalen*, 1881, **210**, 285; Karrer, Staub, and Wälti, *Helv. Chim. Acta*, 1922, **5**, 129).

Hydrolysis of the trimethyl inulin with an aqueous-alcoholic solution of oxalic acid yielded a mixture of trimethyl γ-fructose (trimethyl fructo-furanose) and its ethylfructoside. The homogeneous sugar was obtained from this mixture by further hydrolysis in aqueous solution. Contrary to the observations of Irvine and his co-workers (*loc. cit.*), we have found that the trimethyl γ-fructose yields a crystalline phenylosazone, which is readily obtainable either

as a hydrated form (m. p. 80—82°) or in the anhydrous form (m. p. 137—138°). It was demonstrated that the osazone had retained the three methyl groups which were present in the methylated sugar, *and therefore the positions 1 and 2 in the latter could not* have been occupied by methyl groups.

Oxidation of the trimethyl γ-fructose with nitric acid gave a trimethyl lactol acid (II) which reduced Fehling's solution, and the ethyl ester of this product acquired on further methylation a fourth methyl group. This specimen of a tetramethyl lactol ester did not reduce Fehling's solution, and it was clear that the entry *of the fourth methyl group* had protected the reducing position. The constitution of this product was elucidated by its conversion into a crystalline amide (VI), identical with that isolated by Avery, Haworth, and Hirst (*J.*, 1927, 2308) during the analogous transformation of the tetramethyl γ-fructose isolated from methylated sucrose.



Oxidative degradation of the trimethyl lactol acid (II) by means of acid permanganate led to the isolation of crystalline *d*-trimethyl γ-arabonolactone (III) identical with the specimen previously

obtained by oxidation of tetramethyl γ-fructose (Avery, Haworth, and Hirst) and enantiomorphously related to the specimen prepared from *l*-arabonolactone by Haworth and Nicholson (J., 1926, 1899). It has already been demonstrated that the above *d*-trimethyl γ-arabonolactone yields on further oxidation with nitric acid *l*-dimethoxysuccinic acid (IV), which has been characterised through its crystalline methylamide and by comparison of this with a specimen prepared from *l*-tartaric acid. The above lactone is thus seen to be *d*-2 : 3 : 5-*trimethyl arabonolactone*, and this product can only arise from a trimethyl fructose having methyl groups substituting the corresponding hydroxyl positions in the sugar, and having also a butylene oxide ring. The trimethyl fructose obtained in the above manner by cleavage of trimethyl inulin is thus seen to be 3 : 4 : 6-trimethyl fructose (I), having the oxide ring in the 2 : 5 positions (*i.e.*, adopting the nomenclature of Goodyear and Haworth, J., 1927, 3136, it is 3 : 4 : 6-trimethyl fructo-furanose). From these data, we derive the structure for trimethyl inulin (V) (p. 620).

These experimental results receive a reasonable interpretation only if it be admitted that the γ-fructose residues in inulin are mutually linked through the positions 1 and 2. We therefore derive the general structural formula (VII) for this polysaccharide. The work of Bergmann and Knehe (*Annalen*, 1926, **449**, 302) seems to indicate that triacetyl inulin has a molecular weight corresponding to a triacetyl difructose anhydride, and the latter authors have suggested that inulin may be capable of formulation on this simplified basis. If this be the case, the difructose anhydride which is said to be the unit of triacetyl inulin will receive from our experimental results the formulation (VIII). At this stage we do not, however, commit ourselves to the conclusion that inulin is an associated difructose anhydride, since the problem of the structure of polysaccharides should in our view be capable of solution on general principles of valency distribution. Inulin has probably not fewer than six of the units shown in formula (VII) (or its obvious alternative). Similarly we do not favour the hypothesis that cellulose consists of "associated" units of a di- or tri-glucose anhydride. That principal and not "residual" valency linkings are involved in the union of the component groups of glucose is supported by the evidence of *X*-ray spectrographs of polymeric compounds, and these linkings are analogous to those in, *e.g.*, cellobiose. One of us has already discussed this wider problem in a review of the subject (*Ann. Reports*, 1927, **24**, 81).

EXPERIMENTAL.

Trimethyl Inulin.—Inulin which had been specially purified and finely powdered was converted into the soluble compound with sodium hydroxide by warming in presence of alkali (compare Pfeiffer and Tollens; also Karrer, Staub, and Wälti, *loc. cit.*), and the general procedure adopted for the methylation was similar to that already described by one of us (J., 1915, **107**, 11; 1921, **119**, 198). 35 G. of inulin being dissolved as described above, there were then admitted simultaneously methyl sulphate (20 c.c.) and aqueous sodium hydroxide (50 c.c. of 35%). During this operation, the solution was vigorously stirred and the temperature, which was initially at 30°, was gradually raised to 70° and finally lowered to 30°. The same quantities of these reagents were repeatedly added under identical conditions until 200 c.c. of methyl sulphate and 500 c.c. of the alkali solution had been introduced over a period of two days. The whole of the inulin remained in solution during the course of these operations and at the end the mixture was heated at 100° for ½ hour. The excess of alkali was neutralised in presence of ice by addition of dilute sulphuric acid. To this volume of the aqueous solution half the volume of methylated spirit was added. Sodium sulphate which separated was filtered off and the neutral filtrate was evaporated under diminished pressure to a syrup, which was repeatedly extracted with chloroform. This chloroform solution and the chloroform washings from the sodium sulphate residues were combined and dried over magnesium sulphate. Distillation of the solvent yielded a pale yellow syrup which was completely soluble in methyl iodide. This product was subjected to four further methylations with Purdie's reagents, and was isolated as a white, amorphous powder after each methylation. The final product (32 g.) was washed with ether and dried at 60° in a vacuum. It melted at 138—140° to a colourless liquid which did not immediately solidify on cooling; on heating to 180° it became brown, and it did not appear to suffer much decomposition at 210°. The trimethyl inulin was practically insoluble in water or ether and showed $[\alpha]_D^{20°}$ $-50{\cdot}2°$ ($c = 1{\cdot}61$) in chloroform; it was very soluble in benzene and acetone and moderately easily soluble in alcohol and was devoid of action towards Fehling's solution (Found: C, 53·1; H, 7·75; OMe, 43·5. Calc.: C, 52·9; H, 7·9; OMe, 45·6%). In another preparation 32 g. of inulin were methylated and yielded 29 g. of trimethyl inulin, m. p. 138—140°, $[\alpha]_D^{20°}$ $-49{\cdot}7°$ in chloroform ($c = 2{\cdot}43$).

Hydrolysis. The trimethyl inulin was hydrolysed in lots of 5 g. by digesting it with a solution of 250 c.c. of 70% alcohol con-

taining 2·5 g. of oxalic acid. After heating for 10 hours, the solution attained a constant rotation and was thereupon neutralised by addition of precipitated calcium carbonate. After the mineral salts had been removed by filtration, the filtrate was evaporated under diminished pressure and the syrupy residue extracted with chloroform. The chloroform extract yielded a colourless syrup which reduced Fehling's solution actively, but it was ascertained that this syrup was a mixture of a trimethyl fructose and its ethylfructoside. It was therefore digested for 2 hours at 80° with aqueous hydrochloric acid (0·25%). The mineral acid was neutralised and the solution filtered and evaporated, leaving a residue which was dried and then extracted repeatedly with ether. The ethereal extracts gave on evaporation a faintly yellow syrup (4·25 g.). This distilled as a colourless liquid, b. p. about 115°/0·02 mm., having $n_D^{14°}$ 1·4675; $[\alpha]_D^{20°}$ + 27·7° in chloroform (c = 1·57) (Found: C, 48·45; H, 8·1; OMe, 40·2. $C_9H_{18}O_6$ requires C, 48·6; H, 8·15; OMe, 41·9%). This product was evidently a trimethyl fructose and its properties corresponded to those of a γ-sugar. It decolorised neutral permanganate instantly.

Phenylosazone. The above trimethyl γ-fructose was digested with phenylhydrazine in dilute acetic acid. There separated after heating for ½ hour at 100° an orange-red, viscid syrup, which, after having been washed with water, crystallised immediately from aqueous alcohol in a hydrated form in yellow needles, m. p. 80—82°. Yield, 84% of the theoretical (Found: C, 60·4; H, 7·4; N, 14·0; OMe, 22·2. $C_{21}H_{28}O_4N_4,H_2O$ requires C, 60·3; H, 7·2; N, 13·4; OMe, 22·2%). This hydrated osazone, when gradually heated from 50° to 100° in a high vacuum or when repeatedly crystallised from light petroleum containing a little ether, changed into the anhydrous form, m. p. 137—138°. From the solvent the *osazone* separated as a bright yellow, gelatinous mass of prisms (Found: C, 63·1; H, 7·0; N, 13·9; OMe, 22·6. $C_{21}H_{28}O_4N_4$ requires C, 63·0; H, 7·0; N, 14·0; OMe, 23·3%).

Graded Oxidation of the 3 : 4 : 6-Trimethyl γ-Fructose.—Stage I. Vith nitric acid. This constitution has been ascribed on the basis f the following graded oxidations.

Trimethyl γ-fructose (3 g.) was heated with 18 c.c. of nitric cid (*d* 1·42). The reaction became vigorous at 68° and was later naintained by heating slowly to 95°. The whole operation occupied ½ hours. The solution was now cooled, diluted with water, and vaporated under diminished pressure during constant additions f more water. Finally, the residue was digested with ethyl alcohol, nd the solvent evaporated. The residue was dissolved in ethyl lcohol containing 3% of hydrogen chloride and boiled under

reflux for 6½ hours. After having been neutralised with silver carbonate, the solution was filtered and evaporated under diminished pressure. The syrupy residue was dissolved in ether, filtered from traces of silver, and gave on evaporation a pale yellow syrup which distilled under 0·18 mm. from a bath heated at 132—140°. Yield of distillate, 2·3 g. This showed $n_D^{15°}$ 1·4529; $[\alpha]_D^{16°}$ + 27·1°; OMe, 45·7%. The product reduced Fehling's solution actively and was found by subsequent examination to consist essentially of the ester of the trimethyl lactol acid (II).

This substance was now methylated with Purdie's reagents and gave a mobile liquid which distilled under 0·1 mm. from a bath heated at 115—130°. It showed $n_D^{15°}$ 1·4453; $[\alpha]_D^{15°}$ + 2° (approx.: c = 1·2) in water. Solution of this methylated lactol ester in methyl alcohol and saturation with ammonia at 0° led to the formation after 2 days of the corresponding amide (VI), colourless crystals, m. p. 100—101°, from light petroleum. In admixture with a specimen of the amide prepared by Avery, Haworth, and Hirst (*loc. cit.*) from tetramethyl γ-fructose there was no depression of m. p. (Found: C, 48·2; H, 7·3; N, 5·3. Calc. for $C_{10}H_{19}O_6N$: C, 48·2; H, 7·6; N, 5·6%).

Stage II. With acid permanganate. The ethyl ester of the lactol acid, which reduced Fehling's solution and was isolated as above and as the first product of oxidation of the trimethyl γ-fructose with nitric acid, was now subjected to further oxidation as follows.

The syrupy ester (1·5 g.) was dissolved in 8·4 c.c. of N-sulphuric acid and 8·4 c.c. of water, and the mixture was heated at 85° for 2½ hours in order to hydrolyse the ester. There was then admitted a further quantity of N-sulphuric acid (8·4 c.c.) and the cooled solution was diluted to a volume of 50 c.c. The latter was then titrated slowly with a solution of barium permanganate until manganese oxides began to be precipitated. This required 9·6 c.c. of the permanganate solution (1800 c.c. = 16 g. oxygen). At this stage dilute barium hydroxide solution was admitted until the mixture was alkaline. After having been kept over-night, the mixture was treated with carbon dioxide, and the solids were filtered off and thoroughly washed with water, the washings being added to the filtrate. To the latter N-sulphuric acid was added in sufficient quantity to liberate the whole of the organic acid, which was present as barium salt, and the excess of mineral acid was then neutralised. The filtrate remaining from this treatment was evaporated under diminished pressure and the organic residue was extracted with ether. This appeared to leave a slight residue of a manganese salt of an organic acid, which was subsequently recovered. The ethereal extract yielded a pale yellow mobile

syrup which distilled under 0·12 mm. from a bath heated at 100—115°. This colourless distillate crystallised on being nucleated with a specimen of *d*-2 : 3 : 5-trimethyl γ-arabonolactone which had previously been prepared from tetramethyl γ-fructose by Avery, Haworth, and Hirst (*loc. cit.*). Yield, 0·4 g. This substance, recrystallised from light petroleum, had m. p. 31—32°. The identity of this product with *d*-trimethyl γ-arabonolactone was confirmed by a mixed melting-point determination and by the following analysis (Found: C, 50·4; H, 7·4; OMe, 47·7. Calc.: C, 50·5; H, 7·4; OMe, 48·9%).

The authors have to thank Mr. T. H. Morton, B.Sc., for much assistance in the preparation of trimethyl inulin. They wish to acknowledge also a grant from the Chemical Society which has defrayed part of the cost of this investigation.

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EDGBASTON. [*Received, January 20th*, 1928.]

LXXXIV.—*Some Sulphur Derivatives of Aromatic Methyl Ethers.*

By HERBERT HENRY HODGSON and FREDERICK WILLIAM HANDLEY.

FROM the nitro-*m*-chloroanisoles previously studied (J., 1926, 542), a number of mono- and di-sulphides have been prepared. They give characteristic colours with concentrated sulphuric acid, oleum, and chlorosulphonic acid, and the monosulphides are readily converted into sulphones by treatment with hydrogen peroxide in glacial acetic acid solution.

No trisulphide is formed when sodium trisulphide reacts with 3-chloro-4- or -6-nitroanisole, the disulphide alone being produced in each case (compare Blanksma, *Rec. trav. chim.*, 1901, **20**, 144; Hodgson and Wilson, J., 1925, **127**, 440).

EXPERIMENTAL.

2 : 2'- *and* 4 : 4'-*Diamino*-5 : 5'-*dimethoxydiphenyl Disulphides.*—The corresponding dinitro-compound (4 g.) is boiled under reflux with crystallised sodium sulphide (14 g.) and water (30 c.c.) for 3 hours and the pale brown, filtered solution is exposed to the air; the base then separates (the yield exceeds 90%).

2 : 2'-*Diamino*-5 : 5'-*dimethoxydiphenyl disulphide* crystallises from alcohol (charcoal) in pale yellow needles, m. p. 76° (Found: S, 21·2.

$C_{14}H_{16}O_2N_2S_2$ requires S, 20·8%). Concentrated sulphuric acid, oleum (20%), and chlorosulphonic acid give bluish-green colorations in the cold. Ferric chloride imparts a reddish-purple colour to the solution in alcohol. The *diacetyl* derivative crystallises from dilute acetic acid or alcohol in colourless needles, m. p. 202—203° (Found: S, 16·5. $C_{18}H_{20}O_4N_2S_2$ requires S, 16·3%). The *hydrochloride*, prepared either by passing hydrogen chloride into an alcoholic solution of the base or by dissolving the latter in warm dilute hydrochloric acid (equal parts of concentrated acid and water), separates in colourless needles; on treatment with nitrous acid, it gives *5-methoxybenzene* 2 : 1-*diazosulphide*, which has a characteristic odour and crystallises from alcohol in long, colourless needles, m. p. 80° (Found: N, 17·3; S, 19·6. $C_7H_6ON_2S$ requires N, 16·9; S, 19·3%).

4 : 4'-*Diamino-5 : 5'-dimethoxydiphenyl disulphide* crystallises from alcohol (charcoal) in colourless needles, m. p. 88° (Found: N, 9·4; S, 21·1. $C_{14}H_{16}O_2N_2S_2$ requires N, 9·1; S, 20·8%). Concentrated sulphuric acid, oleum (20%), and chlorosulphonic acid give blue solutions which deepen in colour on warming and become colourless on dilution. Ferric chloride gives a red colour with the alcoholic solution. The *diacetyl* derivative crystallises from dilute acetic acid or alcohol in colourless needles, m. p. 136° (Found: S, 16·6%) The *hydrochloride* is obtained in small, colourless needles and, like its isomeride above, tends to form supersaturated solutions with hydrochloric acid, from which it crystallises with difficulty; it diazotises normally.

2 : 2'- *and* 4 : 4'-*Dinitro-5 : 5'-dimethoxydiphenyl Sulphides*.— (*a*) The disulphide (4 g.), dissolved in warm alcohol (50 c.c.) to which sodium (0·5 g.) had previously been added, was boiled under reflux with the corresponding chloronitroanisole (5 g.) for 8 hours. The separated sulphide was washed with hot alcohol and, after removal of any unchanged chloronitroanisole by steam-distillation, crystallised from glacial acetic acid. The yields were 1·8 g. and 4 g., respectively. (*b*) By Nietzki and Bothof's method (*Ber.* 1894, **27**, 3261) of treating the respective chloronitroanisoles with sodium monosulphide in alcoholic solution. The yields were only 4% and 11%, respectively.

[In the following descriptions the characteristic colours obtained with sulphuric acid, oleum (20%), and chlorosulphonic acid are stated in this order after the analysis in sets of three, each set referring to cold treatment, subsequent warming, and dilution with water.]

2 : 2'-*Dinitro-5 : 5'-dimethoxydiphenyl sulphide* was obtained in stout, yellow needles, m. p. 151° (Found: S, 9·8. $C_{14}H_{12}O_6N$

requires S, 9·5%), which are almost insolnble in alcohol or benzene. Red, reddish-purple, red; brown, reddish-purple, reddish-purple; brown, green, red.

4 : 4′-*Dinitro*-5 : 5′-*dimethoxydiphenyl sulphide* crystallises in colourless micro-needles, m. p. 154° (Found: S, 9·8%). Deep orange, brown, colourless; black, reddish-purple, reddish-purple; black, purple, purple.

The Sulphones of the above Compounds.—The sulphide (1 g.), dissolved in glacial acetic acid (20 c.c.), was treated with hydrogen peroxide (1·5 c.c.; 100 vol.) and heated on the water-bath for 2 hours. On cooling, part of the sulphone crystallised. Waldron and Reid's method (*J. Amer. Chem. Soc.*, 1923, **45**, 2399) proved unsatisfactory for the preparation of these substances.

2 : 2′-*Dinitro*-5 : 5′-*dimethoxydiphenyl sulphone* is practically insoluble in alcohol and benzene, but crystallises from glacial acetic acid in colourless needles, m. p. 182° (Found: C, 45·5. $C_{14}H_{12}O_8N_2S$ requires C, 45·6%). No colour throughout; bright green, violet, red; bluish-green, blue-black, violet.

4 : 4′-*Dinitro*-5 : 5′-*dimethoxydiphenylsulphone* is similar to the above, but less soluble in glacial acetic acid, from which it crystallises in colourless micro-needles, m. p. 245—246° (Found: C, 45·4%). No colour throughout; brown, brownish-purple, brown precipitate; orange, chocolate-brown, brown precipitate.

2- *and* 4-*Nitro*-5-*methoxyphenylmethylsulphones*.—The nitromethoxy-thioether (Hodgson and Handley, *loc. cit.*) (1 g.) in glacial acetic acid (10 c.c.) was heated with hydrogen peroxide (3 c.c.; 100 vol.) for 30 mins. On dilution with water, the sulphone separated as a white, crystalline powder (yield, 1 g. in both cases).

2-*Nitro*-5-*methoxyphenylmethylsulphone* is slightly soluble in hot water, but very soluble in benzene and alcohol, from which it crystallises in colourless needles, m. p. 122° (Found: S, 13·7. $C_8H_9O_5NS$ requires S, 13·8%). Pale yellow, pale yellow, colourless; dark brown, red, yellow; lemon-yellow, reddish-brown, yellow.

4-*Nitro*-5-*methoxyphenylmethylsulphone* is less soluble than its isomeride and crystallises from alcohol in stout prisms, m. p. 130° (Found: S, 13·5%). No colour throughout; orange, purple, yellow; orange, pale yellow, colourless.

2- *and* 4-*Chloro*-5-*methoxythioanisoles*.—The methoxythioanisidine (Hodgson and Handley, *loc. cit.*) was converted by the Sandmeyer method into the chloro-compound, which was removed by steam distillation, and solidified when kept over calcium chloride.

2-*Chloro*-5-*methoxythioanisole* crystallises from light petroleum in stout, colourless needles, m. p. 41° (Found: Cl, 18·7. C_8H_9OClS

requires Cl, 18·8%). Pink, purple, colourless; bluish-green, green, colourless; green, bright blue, colourless.

4-*Chloro-5-methoxythioanisole* crystallises from light petroleum in long, silky needles, m. p. 36° (Found: Cl, 18·9%). Yellow, purple, colourless; yellow, bluish-green, colourless; yellow, green, colourless.

The Action of Sodium Trisulphide on 3-Chloro-4- and -6-nitroanisoles.—A solution of the chloronitroanisole (6 g.) in alcohol (50 c.c.) was mixed with a solution of sodium trisulphide (crystallised sodium sulphide, 3·6 g.; sulphur, 0·96 g.; water, 10 c.c.) and boiled under reflux for 4 hours. The product, after removal of unchanged chloronitroanisole by steam distillation, was crystallised from glacial acetic acid, but no trisulphide was detected, the product being the almost pure disulphide (yield, 4·1 g. and 5·0 g., respectively).

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LXXXV.—*The Origin of the Spectrum of the Glow of Phosphorus.*

By HARRY JULIUS EMELÉUS and ROBERT HENRY PURCELL.

IN a recent paper (J., 1927, 788) the authors described the spectrum produced by passing a discharge through phosphorus pentoxide vapour. It was pointed out that it corresponded in part with the ultra-violet band spectrum of the glow of phosphorus, and the conclusion was drawn that both spectra had their origin in the molecule of an oxide. Dr. R. C. Johnson, to whom we are deeply indebted, has since pointed out to us that the measurements recorded for the discharge through phosphorus pentoxide correspond below 3000 Å. with the bands of the singly ionised oxygen molecule (Johnson, *Proc. Roy. Soc.*, 1924, *A*, **105**, 683); at longer wave-lengths our measurements, which were made on a Hilger small quartz spectrograph, do not furnish a sufficiently accurate basis for comparison. The same spectrum was observed by Stuchtey (*Z. wiss. Phot.*, 1920, **19**, 161) in the thermal decomposition of ozone. From this evidence it might be concluded that the ultra-violet light emission from glowing phosphorus is due to oxygen, a view of considerable interest because of the formation of ozone in the reaction. This idea is based on the identity of the spectra, and since the observations on the phosphorus glow leave much to be desired both in accuracy and in

completeness, owing to the feebleness of the light source, a careful re-examination of the evidence has been made.

A table for comparing the spectroscopic results was constructed from Johnson's measurements and those relating to the glow of phosphorus (Centnerszwer and Petrikaln, *Z. physikal. Chem.*, 1912, **80**, 235; Petrikaln, *Z. Physik*, 1924, **22**, 119; Downey and Emeléus, J., 1924, **125**, 2491; Emeléus and Purcell, *loc. cit.*). Considering first the discharge through phosphorus pentoxide in relation to Johnson's values, the complex band at 3200—3400 Å. is not found in the oxygen spectrum, but at shorter wave-lengths there is close agreement both in the measurements of the main band heads and in their intensities. The last point is well illustrated by the original plates. The oxygen was probably formed by dissociation of the pentoxide. In the glow spectrum none of the bands measured by Johnson in the visible region appears, but, on the other hand, the intense band at 3200—3400 Å. cannot be detected in his plates. At shorter wave-lengths, however, some of the measurements agree with Johnson's, and the general appearance of the two band systems is similar.

The glow spectrum has been produced in other ways which are somewhat difficult to reconcile with the view that it is due to oxygen. For example, it is observed when phosphorus pentoxide is volatilised in the carbon arc or the oxy-hydrogen flame, as well as in the flame of phosphorus. The production of ionised oxygen is, however, thermochemically possible, since the heat evolved in the reaction $2P + \frac{5}{2}O_2 = P_2O_5$ has the remarkably high value of 370 Cal., and the ionisation potential of oxygen is *ca.* 16 volts, which is equivalent to 370 Cal. Little is known of the intermediate reactions leading to the formation of phosphorus pentoxide, but, assuming that a phosphorus pentoxide molecule can transfer its total reaction energy to an oxygen molecule, there is no *à priori* reason why the spectrum of ionised oxygen should not be observed in the arc and flame, as well as in the glow.

Bäckström (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, No. 16) has recently discussed both Stuchtey's work on the thermal decomposition of ozone (*loc. cit.*), and also the oxidation of phosphorus, in the light of a chain-reaction theory of negative catalysis. The luminous oxidation of phosphorus was shown to be accelerated by illumination with a quartz mercury lamp (although the possibility that this effect was due to ozone formation was not considered). This experiment indicated that the oxidation was sensitive to light of the same wave-lengths as it emits, and part of the chemiluminescent light was therefore supposed to be absorbed by molecules of phosphorus (which were shown to absorb light below approx. λ 3000 Å.),

rendering them chemically active, and initiating reaction chains. No assumptions as to the origin of the glow spectrum were, however, involved.

Summarising the present position, our opinion is that the origin of the spectrum of the glow of phosphorus must be regarded as still unsettled, the solution of the problem requiring a more accurate and extensive knowledge of the spectra concerned than is yet available.

Imperial College of Science and Technology,
London, S.W. 7. [*Received, January 10th,* 1928.]

LXXXVI.—*The Introduction of the Triphenylmethyl Group into Phenols.*

By David Runciman Boyd and Douglas Vernon Nelmar Hardy.

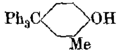
Baeyer and Villiger (*Ber.*, 1902, **35**, 3018) found that phenol and anisole, in the presence of acetic and sulphuric acids, condense with triphenylcarbinol at the ordinary temperature to give 4-hydroxy- and 4-methoxy-tetraphenylmethane respectively. It was afterwards shown by Baeyer (*Ber.*, 1909, **42**, 2624) that 4-hydroxytetraphenylmethane is also formed on warming the deep brown solution which results on dissolving triphenylchloromethane in molten phenol, but that the phenyl ether of triphenylcarbinol is obtained when triphenylchloromethane reacts with potassium phenoxide in the presence of excess of phenol. Gomberg and Kamm (*J. Amer. Chem. Soc.*, 1917, **39**, 2009) have proved that relatively small amounts of hydrogen chloride or of sulphuric acid are sufficient to effect the condensation of triphenylcarbinol with phenol, so that the action of the acids appears to be catalytic.

In studying the properties of triphenylmethoxyphosphorus dichloride (Boyd and Chignell, J., 1923, **123**, 813; Boyd and Smith, J., 1924, **125**, 1477) we observed some time ago that this compound can be used in place of triphenylchloromethane for the preparation of 4-hydroxytetraphenylmethane. Further investigation showed, however, that the reaction has only a limited application as a means of introducing the triphenylmethyl group into phenols. Thus, on heating with *p*-cresol, triphenylmethoxyphosphorus dichloride is converted mainly into triphenylmethane, and on heating with methyl salicylate it yields derivatives of triphenylmethylphosphorous acid. With methyl salicylate the Baeyer–Villiger method also fails, but we have found that condensation in this case can be effected by merely boiling a solution of the carbinol in the ester.

Reaction takes place in the complete absence of any catalytic agency other than the excess of methyl salicylate :

$$Ph_3C{\cdot}OH + C_6H_4(OH){\cdot}CO_2Me = Ph_3C{\cdot}C_6H_3(OH){\cdot}CO_2Me + H_2O.$$

Triphenylcarbinol condenses, under the same conditions, with phenol, but not with *o*-cresol, *m*-cresol, anisole, or *o*-chlorophenol. In the course of our experiments we employed the Baeyer–Villiger method, in a modified form, to condense *o*-cresol with triphenylcarbinol. The product of the reaction was identical with a substance previously obtained by Schorigin (*Ber.*, 1926, **59**, 2502) by heating triphenylchloromethane with a mixture of *o*-cresol and sodium *o*-tolyloxide. On grounds which appear to us to be inadequate, Schorigin regards this compound, not as 4-hydroxy-3-methyltetraphenylmethane (I), but as ααα-triphenyl-β-2-hydroxyphenylethane (II). In a more recent paper (*Ber.*, 1927, **60**, 2373) Schorigin describes experiments on the condensation of triphenylcarbinol with cresols by the Baeyer–Villiger method. In this way he has prepared from triphenylcarbinol and *m*-cresol a condensation compound which he considers to be a tetraphenylmethane derivative (III or IV). With *p*-cresol, in the presence of acetic and sulphuric acids, triphenylcarbinol is converted into triphenylmethane; but a condensation product, to which he assigns formula (V), has been obtained by Schorigin by heating triphenylchloromethane with sodium *p*-tolyloxide and *p*-cresol.



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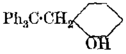

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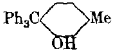

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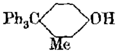

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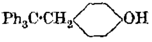

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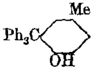


(VI.)

Schorigin bases his formulæ for the *o*- and *p*-cresol condensation products mainly on the fact that, whereas he was able to obtain triphenylcarbinol in small quantity on oxidising the *o*- and *p*-cresol derivatives with chromic anhydride, no triphenylcarbinol could be isolated on treating either the *m*-cresol derivative or 4-hydroxytetraphenylmethane with the same oxidising agent. Since Gomberg and Cone (*Ber.*, 1906, **39**, 1464) have shown that unsymmetrical tetraphenylethane gives triphenylcarbinol on oxidation with chromic anhydride, it is argued that the *o*- and *p*-cresol condensation compounds are derivatives of this hydrocarbon, and that the *m*-cresol compound is derived from tetraphenylmethane.

Several observations which we have made are, however, opposed to the view that the *o*- and *p*-cresol compounds differ in type from the *m*-cresol derivative and 4-hydroxytetraphenylmethane :

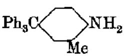
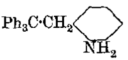
(1) The four compounds behave similarly on distillation with soda-lime; each gives triphenylmethane.

(2) From their behaviour on heating with a mixture of hydriodic and acetic acids they fall into two groups, but not the groups which are to be expected on the basis of Schorigin's views. The *o*- and *m*-cresol compounds behave similarly, yielding triphenylmethane, whereas the *p*-cresol derivative and 4-hydroxytetraphenylmethane are both stable towards this reducing agent.

(3) Although on oxidising with chromic anhydride, Schorigin failed to obtain triphenylcarbinol from 4-hydroxytetraphenylmethane and its homologue derived from *m*-cresol, we have found that the carbinol can be obtained from each of the four compounds by merely warming with sulphuric acid.

The weight of evidence appears to us, therefore, to be against the view that the *o*- and *p*-cresol derivatives differ fundamentally in constitution from the *m*-cresol derivative and the unsubstituted hydroxytetraphenylmethane, and we consider that, until definite proof to the contrary has been brought forward, the *o*- and *p*-cresol compounds should be represented by formulæ (I) and (VI) respectively.

The adoption of formula (I) for the *o*-cresol derivative of triphenylcarbinol necessitates a corresponding alteration in the formula of the condensation product obtained from triphenylcarbinol and *o*-toluidine hydrochloride (van Alphen, *Rec. trav. chim.*, 1927, **46**, 501). Since the *o*-toluidine derivative can be converted into compound (I) by diazotisation, it follows that formula (VII) must be assigned to it; and not, as van Alphen suggests, formula (VIII) :

(VII.)   (VIII.)

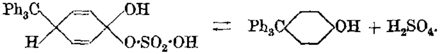
Our observations on the action of sulphuric acid upon 4-hydroxytetraphenylmethane and its derivatives show that the Baeyer–Villiger reaction is reversible; and in this connexion it is of interest to consider the mechanism of the process. An acetic–sulphuric acid solution of triphenylcarbinol is orange-red, and doubtless contains triphenylmethyl sulphate, ionised to a certain extent :

$$Ph_3C{\cdot}OH + H_2SO_4 \longrightarrow Ph_3C{\cdot}O{\cdot}SO_2{\cdot}OH \rightleftharpoons Ph_3\overset{+}{C} + SO_4\overset{-}{H}.$$

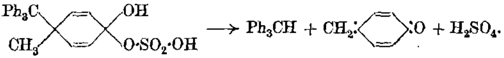
If to this orange solution a phenol, or its methyl ether, is added, a deep brown colour is immediately produced. This we

attribute to the formation of a quinonoid addition compound, the ions of triphenylmethyl sulphate being added to the 1 : 4-positions of the phenolic nucleus :

In the normal reaction this complex gradually breaks up into sulphuric acid and the tetraphenylmethane derivative :



This hypothesis explains the rôle of the sulphuric acid, and the reversibility of the reaction. With *p*-cresol, however, the decomposition of the complex cannot proceed in the way indicated in the above equation, owing to the blocking of the position para to the hydroxyl group. In place of a condensation compound, triphenylmethane is formed; the other product being not improbably, as Schorigin has suggested, a polymerised form of *p*-quinomethane :



The action of phenols upon triphenylchloromethane and upon triphenylmethoxyphosphorus dichloride may be explained in a similar fashion (compare Busch and Knoll, *Ber.*, 1927, **60**, 2243). But whereas in the Baeyer–Villiger reaction the dissociating solvent is the mixture of acetic and sulphuric acids, here it is the phenol itself which performs this function. It follows that where the phenol has a low ionising power no ionisation may result and therefore no colour be developed, *e.g.*, with methyl salicylate and guaiacol. The appearance of a brown colour, and the accompanying acceleration of the reaction, which Baeyer observed (*loc. cit.*) on adding stannic chloride to the colourless solution of triphenylchloromethane in guaiacol, are doubtless due to the formation of the double salt $Ph_3CCl,SnCl_4$, which readily dissociates into ions, thus enabling the quinonoid complex to be formed.

The data recorded in the following table show that the stability of the tetraphenylmethane molecule towards reagents, such as sulphuric and hydriodic acids, which promote fission, is altered markedly by the presence of substituent groups, and that the influence of a substituent is dependent both on its chemical nature and on its position in the molecule.

Tetraphenylmethane Derivatives.

	Action of sulphuric acid.				
	Wt. (g.).	Temp.	Time (mins.).	Yield of $Ph_3C\cdot OH$.	Action of hydriodic–acetic acid.
4-Hydroxy-	2	60°	30	0·1	Stable.
4-Methoxy-	1	50	15	0·22	4-Hydroxytetraphenylmethane.
4-Hydroxy-3-methyl-	1	40	10	0·26	Ph_3CH.
4-Methoxy-3-methyl-	2	40	5	1·15	,,
4(2)-Hydroxy-2(4)-methyl-	1	50	30	0·05	,,
2-Hydroxy-5-methyl-	1	40	30	0·05	Stable.
4-Hydroxy-3-carboxy-	1	40	10	Nil	,,

The study of the tetra-arylmethane group of compounds from this point of view is being continued.

EXPERIMENTAL.

The Direct Action of Triphenylcarbinol upon Phenols.—4 G. of triphenylcarbinol and 5 g. of phenol were heated to boiling for about an hour, the mixture becoming almost completely solid. After cooling, the mass was boiled with dilute caustic soda solution to remove the excess of phenol, and the solid 4-hydroxytetraphenylmethane filtered off. After washing and drying, it crystallised from acetic acid in white flakes, m. p. 282°. The yield was 5·0 g., 97% of the theoretical. The compound was identified by the melting point of a mixture with an authentic specimen and by conversion into its acetyl derivative, m. p. 175°, as recorded by Baeyer.

4-*Hydroxytetraphenylmethane*-3-*carboxylic Acid*, $CPh_3\cdot C_6H_3(OH)\cdot CO_2H$.—4 G. of triphenylcarbinol and 5 g. of methyl salicylate were gently boiled under reflux. Water vapour was continuously evolved for about an hour; the mixture was then allowed to cool. The excess of methyl salicylate was hydrolysed by boiling with 40 c.c. of alcohol and 3 g. of caustic potash for 2 hours under reflux. The alcohol was then evaporated, the residue boiled with water, and the insoluble matter filtered off. After drying, the product (5·2 g.) was boiled with a mixture of 20 c.c. of acetic acid and 5 c.c. of hydriodic acid for 2 hours. On cooling, almost colourless crystals of the carboxylic acid separated together with some triphenylmethane. The crystals were collected and washed with sulphurous acid to remove iodine. The dried material crystallised from petroleum (b. p. 100—120°) in colourless needles, m. p. 232°. The yield was 1·9 g. (Found: C, 82·2; H, 5·5. $C_{26}H_{20}O_3$ requires C, 82·0; H, 5·3%).

When the acid was heated above its melting point, carbon dioxide was evolved and a white sublimate obtained, which was identified as

4-hydroxytetraphenylmethane by its melting point (276—282°), mixed-melting point (278—282°), and by conversion into 4-acetoxytetraphenylmethane (m. p. 173—175°). 4-Hydroxytetraphenylmethane-3-carboxylic acid is insoluble in aqueous alkalis; with an alcoholic solution of sodium hydroxide it gives a sodium salt.

4-Acetoxytetraphenylmethane-3-carboxylic Acid,
$CPh_3{\cdot}C_6H_3(OAc){\cdot}CO_2H$.—
1 G. of the hydroxy-acid was boiled with 10 c.c. of acetic anhydride and 3 g. of anhydrous sodium acetate for 2 hours. The solid left after the mixture had been diluted with water and boiled was filtered off, washed, and dried. It crystallised from acetone–light petroleum as a white powder, m. p. 210° (Found: C, 79·5; H, 5·5. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·25%). The acid is insoluble in aqueous alkalis.

5-Bromo-4-hydroxytetraphenylmethane-3-carboxylic Acid,
$CPh_3{\cdot}C_6H_2Br(OH){\cdot}CO_2H$.—
2 G. of the hydroxy-acid, 1 g. of bromine, and 15 c.c. of acetic acid were boiled under reflux until evolution of hydrogen bromide ceased. On cooling, the *bromo*-compound separated in colourless prisms, m. p. 239° after recrystallisation from acetic acid (Found: Br, 17·2. $C_{26}H_{19}O_3Br$ requires Br, 17·4%). Like the parent substance, the bromo-acid is insoluble in aqueous alkalis.

5-Nitro-4-hydroxytetraphenylmethane-3-carboxylic Acid,
$CPh_3{\cdot}C_6H_2(NO_2)(OH){\cdot}CO_2H$.—
2 C.c. of nitric acid were added to a mixture of 2 g. of the hydroxy-acid and 50 c. c. of acetic acid, and the whole kept for 24 hours with frequent shaking. All the hydroxy-acid had then dissolved. The solution was poured into water and the resulting yellow precipitate was collected and dried. After crystallisation from light petroleum and then from benzene, the substance formed light yellow needles, m. p. 226° (Found: N, 3·2, 3·6. $C_{26}H_{19}O_5N$ requires N, 3·3%). The nitro-acid dissolves readily in dilute caustic soda solution, from which it is precipitated on acidification.

The Action of Triphenylmethoxyphosphorus Dichloride upon Phenols.—(1) *Phenol.* 5 G. of triphenylmethoxyphosphorus dichloride were added to 5 g. of molten phenol. The dichloride dissolved slowly with production of an intense red-brown colour, and at the same time hydrogen chloride was evolved. After standing for 20 minutes with stirring, the mixture was heated to 120°. The colour then rapidly faded, and after heating for 30 minutes the product consisted of a light brown solid. When cold, this was boiled with dilute caustic soda solution, and the insoluble material was collected, washed, and dried. After crystallisation from alcohol it melted at 282°. The yield was 3·5 g. (87%). The identity of the

product as 4-hydroxytetraphenylmethane was shown by a mixed melting point determination and by acetylation. On acidifying the caustic soda solution, 0·18 g. of a phosphorus-containing acid was obtained.

(2) m-*Cresol*. A mixture of 2 g. of the phosphorus dichloride and 2 g. of *m*-cresol was gradually warmed in an oil-bath. A brown colour developed slowly, and faded to a pale brown when the temperature was raised to 120°. After cooling, the excess of *m*-cresol was removed by treatment with caustic soda, and the residue was dissolved in ether and shaken with caustic soda. The resulting white gelatinous precipitate was washed with ether and boiled with hydrochloric acid. The product, after crystallisation from acetic acid, melted at 213° and weighed 0·44 g. Mixed with 4(2)-hydroxy-2(4)-methyltetraphenylmethane, it melted also at 213°. From the ethereal solution there were obtained a phosphorus-containing oil and 0·32 g. of triphenylmethane, identified by a mixed melting point determination and by conversion into the benzene compound (m. p. 78°).

(3) p-*Cresol*. 5 G. of the phosphorus dichloride and 5 g. of *p*-cresol were heated together in an oil-bath. The mixture gradually became brown and hydrogen chloride was evolved. The temperature was maintained at 100° and the colour changed to wine-red. When cold, the unchanged *p*-cresol was removed in the usual manner with caustic soda; on acidification of the alkaline filtrate a very small amount of a phosphorus-containing acid, mixed with a little red, amorphous colouring matter, was precipitated. The insoluble portion was crystallised from alcohol. After 2·45 g. of triphenylmethane had separated, the mother-liquor deposited 0·5 g. of a phosphorus-containing substance. This crystallised from alcohol in colourless prisms, m. p. 179—180°, and from its analysis appeared to be the *di*-p-*tolyl ester* of *triphenylmethylphosphorous acid* (Found: C, 78·6; H, 6·1; P, 6·0. $C_{33}H_{29}O_3P$ requires C, 78·55; H, 5·8; P, 6·2%).

The Action of Triphenylcarbinol upon Phenols in the Presence of Sulphuric Acid.—In carrying out these experiments the amounts of acetic and sulphuric acids employed were considerably less than those used by Baeyer and Villiger. As a result the products were more readily isolated.

(1) o-*Cresol*. 6 G. of triphenylcarbinol and 6 g. of *o*-cresol were dissolved in 60 c.c. of acetic acid by warming, and 10 g. of pure sulphuric acid were then added. The intense brown solution was kept until the following day; the colour had then faded to a pale red-brown. The solution was poured into water, and the precipitated material boiled with caustic soda solution. After drying, the

product was crystallised by dissolving it in a little benzene and adding hot methyl alcohol to the filtered solution. White, powdery crystals separated, m. p. 180—181°. The yield was 8·1 g. By dissolution in Claisen's solution (*Annalen*, 1919, **418**, 96) and subsequent crystallisation, the melting point was raised to 183° (Schorigin originally gave 183°, but in his most recent paper gives 186°). Mixed with a specimen of Schorigin's "cryptophenol," prepared from sodium *o*-tolyloxide and triphenylchloromethane, it melted also at 183°. Further evidence of identity was obtained by converting the two products into their acetyl derivatives.

4-*Acetoxy-3-methyltetraphenylmethane*, $CPh_3 \cdot C_6H_3Me \cdot OAc$.—1 G. of 4-hydroxy-3-methyltetraphenylmethane, 1 g. of anhydrous sodium acetate, and 10 c.c. of acetic anhydride were refluxed together for 2 hours. The mixture was poured into water and the precipitated solid was collected, dried, and crystallised from benzene and methyl alcohol. The substance forms colourless prisms, m. p. 150°. The yield was 0·8 g. (Found: C, 85·7; H, 6·3. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·2%).

4-*Methoxy-3-methyltetraphenylmethane*, $CPh_3 \cdot C_6H_3Me \cdot OMe$.—The *methyl o-tolyl ether required for this preparation* was made by warming 11 g. of *o*-cresol in a solution of caustic soda (16 g. in 20 c.c. of water) to 40°, and adding 25 g. of methyl sulphate in small portions, the mixture being well shaken after each addition. The oil was extracted with ether, shaken with caustic soda, and dried over sodium sulphate. After removal of the ether and distillation, 8·8 g. of the pure substance were obtained.

9 G. of methyl *o*-tolyl ether and 6 g. of triphenylcarbinol were dissolved in 60 c.c. of acetic acid, and 12 g. of pure sulphuric acid were added. The dark brown solution, after 24 hours, deposited a considerable amount of crystals, which were filtered off after 48 hours and washed, first with acetic acid and then with alcohol. The yield was 8·56 g. (The mother-liquor may be used for a second preparation by merely dissolving a further quantity of triphenylcarbinol in it.) The compound crystallises from acetic acid or acetone in white, spherical aggregates, m. p. 165°. Its constitution was established by analysis (Found: C, 88·9; H, 6·4. $C_{27}H_{24}O$ requires C, 89·0; H, 6·6%), and by its preparation by direct methylation of 4-hydroxy-3-methyltetraphenylmethane. 2 G. of 4-hydroxy-3-methyltetraphenylmethane were dissolved in 20 c.c. of benzene, and shaken with 50 c.c. of Claisen's solution. To this mixture, 2 g. of methyl sulphate were added, and the whole was well shaken for 15 minutes. The benzene layer was separated, washed with a little of Claisen's solution and then with water, and evaporated to a small bulk. The addition of alcohol caused the separation of

brownish crystals, m. p. 162—165°. On recrystallisation the product melted at 165°, and gave the same melting point when mixed with some of the previously prepared material.

3-*Bromo*-4-*methoxy*-5-*methyltetraphenylmethane*, $CPh_3{\cdot}C_6H_2MeBr{\cdot}OMe$.— 2 G. of 4-methoxy-3-methyltetraphenylmethane were boiled with 20 c.c. of acetic acid and 1 g. of bromine until evolution of hydrogen bromide ceased. On cooling, 2·2 g. of colourless crystals separated. These crystallised from acetic acid in prisms, m. p. 180°, with a little previous shrinkage (Found: Br, 18·15. $C_{27}H_{23}OBr$ requires Br, 18·0%).

(2) m-*Cresol*. 6 G. of triphenylcarbinol and 6 g. of *m*-cresol were dissolved in 60 c.c. of acetic acid, and 10 g. of sulphuric acid were added. After standing 24 hours, 5·0 g. of the condensation product were filtered off, and several days later a further quantity, 2·3 g., was obtained. The melting point after two recrystallisations from acetic acid was 213—214° as recorded by Schorigin.

The Action of Hydriodic Acid upon 4-*Hydroxytetraphenylmethane and its Derivatives*.—0·5 G. of each compound was boiled with a mixture of 4 c.c. of hydriodic acid and 8 c.c. of acetic acid for 3 hours. In those cases where fission occurred, the substance dissolved fairly rapidly and triphenylmethane separated as an oil on the surface of the liquid, the action being completed in 30 minutes. The yield of triphenylmethane was practically theoretical. Where the tetraphenylmethane compound was stable, the material never passed completely into solution, and on cooling and filtering, almost the whole amount was recovered unchanged. The acetic acid filtrate was poured into water and the minute amount of material precipitated was carefully examined, but no trace of triphenylmethane could be detected.

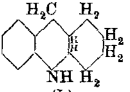
The Action of Sulphuric Acid upon 4-*Hydroxytetraphenylmethane and its Derivatives*.—A mixture of the substance with pure sulphuric acid (10 c.c. for 1 g.) was gently warmed as recorded in the table on p. 634. At the end of the time practically all (in most cases all) the substance had dissolved and the solution was coloured orange. The white precipitate produced on pouring this solution into water was extracted with benzene, the benzene layer washed with dilute caustic soda solution and with water, and the benzene evaporated. The residue was weighed after recrystallisation from light petroleum. It was identified as triphenylcarbinol by its melting point and by a mixed melting point determination.

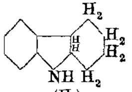
UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, January 14th*, 1928.]

LXXXVII.—*Stereoisomerism in Polycyclic Systems. Part IV. Two Stereoisomerides of* 2:3:4:5:12:13-*Hexahydroquinindene.*

By William Henry Perkin, jun., and Sydney Glenn Preston Plant.

In the earlier investigations it has been shown that octahydroacridine (I) (Perkin and Sedgwick, J., 1924, **125**, 2437; 1926, 438) and hexahydrocarbazole (II) (Gurney, Perkin, and Plant, J., 1927, 2676)* each occur in two stereoisomeric modifications the existence of which can be accounted for by the Sachse–Mohr theory of multiplanar rings. It was found that when tetrahydrocarbazole is reduced to hexahydrocarbazole the product consists almost entirely of the *cis*-modification, only about 1—2% of the *trans*-form being present. In Part III it is pointed out that this may be ascribed to the fact that in the configuration of the reduced dicyclic system of the *trans*-modification there must be considerable strain. It is obvious, however, that in these cases the effect of the benzene ring must also be considered, and the factors which determine the relative strain in the various stereoisomerides of this type are clearly more complex than in a simple dicyclic system. With a view to gaining information bearing on this point, we have decided to examine the possibility of stereoisomerism in the case of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (III).†


(I.)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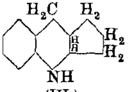
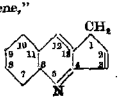

(III.)

This substance is closely allied to hexahydrocarbazole, the possibility of stereoisomerism being again a feature of the dicyclic system composed of one 6-membered and one 5-membered ring, and it might be expected from previous experience in the case of the

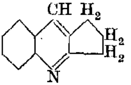
* These communications are regarded as Parts I, II, and III, respectively, of this series.

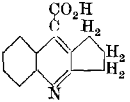
† It has been suggested by Dr. Smith that compounds containing the ring system present here should be considered as derived from the hypothetical parent substance, "quinindene,"



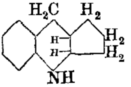
reduction of tetrahydrocarbazole that only a small quantity of the *trans*-form would occur in any reaction which might give rise to both stereoisomerides at the same time.

We have prepared considerable quantities of 2 : 3-dihydroquinindene (IV) from 2 : 3-dihydroquinindene-12-carboxylic acid (V) by the elimination of carbon dioxide (compare Borsche, *Annalen*,

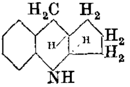
(IV.) 

 (V.)

1910, **377**, 120), and have investigated its reduction by means of tin and hydrochloric acid in aqueous-alcoholic solution, under conditions similar to those used in the case of hexahydrocarbazole. An oily mixture of the *cis*- and *trans*-bases was obtained, and it was found that separation could best be brought about by converting the product into the mixture of the corresponding benzoyl derivatives and separating these by fractional crystallisation from alcohol and acetone. In this way two stereoisomeric *5-benzoyl-2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindenes*, (A), m. p. 174°, and (B), m. p. 161°, were isolated, but contrary to the experience in the case of the reduction of tetrahydrocarbazole, where only 1—2% of the *trans*-form is obtained, the proportion of (A) to (B) is about 1 to 3. The corresponding stereoisomeric 2 : 3 : 4 : 5 : 12 : 13-*hexahydroquinindenes* (VI and VII) have been isolated from these benzoyl compounds by hydrolysis, (A) melting at 67°, and (B) being an oil, b. p. 284°/



cis- (VI.)



trans- (VII.)

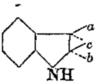
762 mm.. Each base has been converted into its *acetyl* derivative, that from (A) melting at 102°, and that from (B) at 87°. The *picrate* of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (A) melts at 193° (decomp.), and that of the stereoisomeride (B) at 158°. Both of the isomeric benzoyl derivatives have been shown to be unimolecular.

The nature of the reducing agent influences the course of the reaction, since in subsequent experiments, when 2 : 3-dihydroquinindene was reduced electrolytically and the product separated as before by means of the benzoyl derivatives, appreciable quantities of both forms, (A) and (B), were again isolated, but the proportion

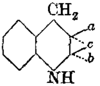
of the benzoyl derivative (A) (m. p. 174°) to (B) (m. p. 161°) was now about 1 to 12. It is an interesting fact that our experiments seem to show that the electrolytic reduction of tetrahydrocarbazole gives no appreciable quantity of the *trans*-hexahydrocarbazole.

The two stereoisomeric 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindenes have here been designated (A) and (B), respectively. As will be pointed out later, considerations of strain and of the relative amounts of the two forms produced lead to no certain indication as to which is the *cis*- and which the *trans*-modification. There is no absolute method available for determining this point, since oxidation to some simple recognisable *cis*- and *trans*-forms of a monocyclic system, or synthesis from these, seems to be out of the question.

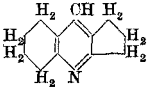
It is clear that the factors which determine the relative amounts of the two stereoisomerides in the cases so far investigated are numerous and complex. The nature of, and the strain in, the ring system undergoing reduction, the kind of reducing agent used, and the relative strains in each of the isomeric products will all presumably have some influence on the proportion of the stereoisomerides formed. A detailed study of the problem of the strain in the products is very interesting in view of the different nature of the results already obtained on reducing tetrahydrocarbazole and 2 : 3-dihydroquinindene to hexahydrocarbazole and 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene, respectively. Adopting the generally accepted views (i) that the normal position of the benzene ring is in one plane with the six hydrogen atoms symmetrically arranged in the same plane, (ii) that the 5-membered ring is also normally uniplanar, and (iii) that the *cyclo*hexane ring has one of the well-known multiplanar configurations, it is possible with the aid of models to see that the *trans*-valencies, marked *a* and *b* in the dihydroindole skeleton (VIII), when projected on to a plane at right angles to the line joining the two carbon atoms to which they are attached, enclose a relatively large angle (about 110°), so that a *trans*-union of the remaining $-(CH_2)_4-$ group to form hexahydrocarbazole results in a very highly strained configuration. The dihydroindole skeleton is itself strained and presumably uniplanar, and any attempt to facilitate the *trans*-union of the $-(CH_2)_4-$ group by reducing the angle



(VIII.)



(IX.)



(X.)

between the *trans*-valencies *a* and *b* by free rotation results in an increased strain in this section. The corresponding projections of

the *cis*-valencies, *a* and *c*, are coincident, and the *cis*-hexahydrocarbazole molecule is far less strained than the *trans*-. There can be little doubt that the formation of only very small quantities of *trans*-hexahydrocarbazole during the reduction of tetrahydrocarbazole is due in a large measure to this fact.

Applying the same considerations to the case of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene, it is found that the effect of the benzene ring is to alter the positions in the multiplanar, 6-membered ring so as to cause the two *trans*-valencies, *a* and *b* in fig. IX, to be so situated that, when projected on to a plane as before at right angles to the line joining the two carbon atoms to which they are attached, they enclose only a small angle. The study of the model indicates that the angle enclosed between the projections of the corresponding *cis*-valencies, *a* and *c*, is approximately the same as in the case of the *trans*-. It will be apparent, therefore, that both the *cis*- and the *trans*-union of the remaining $-(CH_2)_3-$ group to complete the 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene molecule should be brought about with approximately equal ease. It is also apparent that the size of the angle enclosed between the projections of the various *cis*- and *trans*-valencies on to a plane perpendicular to that already considered will have a marked effect upon the strains in the completed molecules, but this angle varies only slightly in the systems under consideration. The effect of this factor will, of course, depend upon the number of carbon atoms in the groups $-(CH_2)_n-$ which are attached to these valencies in order to complete the tricyclic system.

In the absence of quantitative data concerning the actual distribution of the total strain throughout these molecules, it is difficult at present to be more definite, but it is even possible that the *cis*-modification of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene may be more strained than the *trans*-. These facts are interesting in view of the isolation of considerable quantitites of both forms of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene as the result of the reduction of 2 : 3-dihydroquinindene. We propose to extend these investigations to other polycyclic systems with a view to obtaining further data which may be useful for developing more definite ideas concerning some of the points raised above.

The reduction of dihydroquinindene has previously been investigated by von Braun, Petzold, and Schultheiss (*Ber.*, 1923, **56**, 1347). By catalytic hydrogenation these authors obtained two products, one of which could be benzoylated, but the other could not. These substances are regarded by them as 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (III) and "2 : 3-trimethylene-5 : 6-tetramethylenepyridine" (X), respectively; the former is described as an oil, b. p. 169—171°/18 mm., its benzoyl derivative is said to melt at 157° and

its picrate at 154°. It seems probable that this substance is identical with the 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (B) described in this communication.

Experimental.

A mixture of isatin (50 g.), *cyclo*pentanone (90 g.), aqueous potassium hydroxide (200 c.c. of 30%), and alcohol (400 c.c.) was boiled under reflux for 8 hours, the alcohol removed by distillation, the residue diluted by water (about 2500 c.c.), and acidified, after filtering, with an excess of glacial acetic acid. The 2 : 3-dihydroquinindene-12-carboxylic acid (V), which rapidly separated, was used without further purification for the preparation of 2 : 3-dihydroquinindene, but it can be crystallised from glacial acetic acid and obtained in pale green prisms, m. p. 297° (decomp.) (Found : N, 6·5. Calc. : N, 6·6%. Compare Borsche, *loc. cit.*, who gives the m. p. 277—278°). The dry, crude acid was heated at a temperature just above its m. p. in a small distillation flask for about 10 minutes, until the evolution of carbon dioxide ceased, and the residue was then distilled under reduced pressure. The distillate was dissolved in ether and shaken with dilute aqueous sodium carbonate, the ethereal solution was dried over potassium carbonate, the solvent removed, and the residue crystallised from low-boiling petroleum, from which 2 : 3-dihydroquinindene separated in large, colourless prisms, m. p. 60° (compare Borsche, *loc. cit.*). The yield from 50 g. of isatin amounted to 23 g.

Reduction of 2 : 3-Dihydroquinindene with Tin and Hydrochloric Acid.—A mixture of 2 : 3-dihydroquinindene (17·5 g.), alcohol (70 c.c.), concentrated hydrochloric acid (70 c.c.), and granulated tin (70 g.) was boiled under reflux on the steam-bath for 5 hours and then filtered while still hot, the tin residues being washed with a little hot alcohol. After removal of the alcohol by distillation, the residue was cooled, treated gradually with an excess of concentrated aqueous sodium hydroxide (70 g. of NaOH), and extracted several times with ether. The extract was dried over potassium carbonate and the solvent removed, a mixture of products being obtained as an oil which did not solidify after standing for some time. The mixture was converted into the corresponding benzoyl derivatives by shaking with benzoyl chloride (20 g.) and an excess of dilute aqueous sodium hydroxide, the product soon separating in a solid condition. On crystallising this mixture from alcohol, a quantity of *5-benzoyl-2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene* (A) separated first in long, colourless prisms, m. p. 174° (Found : C, 82·1 ; H, 7·0 ; *M*, by Rast's method, 289. $C_{19}H_{19}ON$ requires C, 82·3 ; H, 6·8% ; *M*, 277). After a short time the second derivative also began to separate at a

point very easily detected, and the solution was then rapidly filtered. The mixture which crystallised from the filtrate was then recrystallised *from acetone, 5-benzoyl-2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene* (B) separating first in large, stout, colourless prisms, m. p. 161° (Found : C, 82·4 ; H, 7·0% ; *M*, by Rast's method, 261). After a time the other benzoyl derivative (m. p. 174°) also began to separate from this solution, and at this point the product was collected. Both of these stereoisomerides can be purified, if necessary, by further recrystallisation from either alcohol or acetone. After a certain quantity of each stereoisomeride had been isolated in this way, the mother-liquors were united and the mixture was obtained by dilution with water or by evaporation of the solvent, and again subjected to the above process of separation. The whole procedure can be repeated to bring about complete separation, and the amounts of the stereoisomerides (B) and (A) were found to be approximately in the ratio 3 : 1, although in different preparations the actual amounts varied a little. These benzoyl derivatives are only slowly hydrolysed by aqueous-alcoholic potassium hydroxide, prolonged boiling being necessary in order to separate the corresponding bases.

2 : 3 : 4 : 5 : 12 : 13 - Hexahydroquinindene (A).—5 - Benzoyl - 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (A) (4 g.) was boiled under reflux with potassium hydroxide (25 g.) in aqueous alcohol for 24 hours, the alcohol was distilled off, and the residue was shaken with ether and water. Two clear layers were obtained in this case. The ethereal layer was shaken with dilute hydrochloric acid and no residue remained after evaporation of the ether, so that hydrolysis of the benzoyl derivative was complete. The solution of the base in dilute hydrochloric acid was made alkaline with ammonia and extracted with ether, the ethereal solution dried over potassium carbonate, and the solvent removed. The residual oil quickly solidified, and, after crystallisation from petroleum, 2 : 3 : 4 : 5 : 12 : 13-*hexahydroquinindene* (A) was obtained in large, colourless prisms, m. p. 67° (Found : C, 83·5; H, 8·6. $C_{12}H_{15}N$ requires C, 83·2 ; H, 8·7%). By shaking this base (A) with benzoyl chloride and dilute aqueous sodium hydroxide the benzoyl derivative (m. p. 174°) was regenerated. After boiling the mixture of the base with an excess of acetic anhydride for 20 minutes, shaking it with water, and crystallising the product from dilute alcohol, 5-*acetyl*-2 : 3 : 4 : 5 : 12 : 13-*hexahydroquinindene* (A) was obtained in long, colourless prisms, m. p. 102° (Found : N, 6·4. $C_{14}H_{17}ON$ requires N, 6·5%). The *picrate* of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (A) separated from alcohol in small, yellow prisms, m. p. 193° (decomp.).

2 : 3 : 4 : 5 : 12 : 13-*Hexahydroquinindene* (B).—A mixture of 5-benzoyl-2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (B) (7·5 g.) and potassium hydroxide (25 g. in aqueous alcohol) was boiled under reflux for 24 hours, the alcohol was distilled off, and the residue well shaken with ether and water. The ethereal layer, after being filtered from some unchanged benzoyl derivative, which is only slightly soluble in ether, was extracted with dilute hydrochloric acid, and then, after removal of the ether, a further quantity of unchanged benzoyl derivative was obtained. The total quantity of benzoyl compound recovered amounted to 3·5 g. The hydrochloric acid solution of the base was made alkaline with ammonia and extracted with ether, the ethereal solution was dried over potassium carbonate, and the solvent removed. The residual oily 2 : 3 : 4 : 5 : 12 : 13-*hexahydroquinindene* (B) has not been made to solidify, but, on distillation, it boiled at 284°/762 mm. (Found: C, 83·4; H, 8·7. $C_{12}H_{15}N$ requires C, 83·2; H, 8·7%). By shaking the base (B) with benzoyl chloride and dilute aqueous sodium hydroxide the benzoyl derivative (m. p. 161°) was obtained. After a solution of the base in an excess of acetic anhydride had been boiled for 20 minutes and shaken with water, and the solid crystallised from low-boiling petroleum, 5-*acetyl*-2 : 3 : 4 : 5 : 12 : 13-*hexahydroquinindene* (B) separated in colourless plates, m. p. 87° (Found: C, 78·0; H, 8·0. $C_{14}H_{17}ON$ requires C, 78·1; H, 7·9%). The *picrate* of 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindene (B) separated from alcohol in orange-coloured prisms, m. p. 158°.

Electrolytic Reduction of 2 : 3-*Dihydroquinindene.*—2 : 3-Dihydroquinindene (8 g.) was dissolved in dilute sulphuric acid (300 c.c. of 10%) and reduced electrolytically, lead electrodes and a current of 2·5 amps. (0·01 amp. per sq. cm. of cathode) being used, for 16 hours. The solution was then filtered, made alkaline with aqueous sodium carbonate, and extracted with ether. After the extract had been dried over potassium carbonate and the solvent removed, the residual oil was distilled under reduced pressure, and the distillate was collected at 155—160°/11 mm. This mixture of the 2 : 3 : 4 : 5 : 12 : 13-hexahydroquinindenes (A) and (B) was converted by benzoylation in the usual way into the two corresponding stereoisomeric benzoyl derivatives (A) and (B). On fractional crystallisation from alcohol a considerable amount of the isomeride (B) separated first in this case, since it was present to a greater extent than in the product from the reduction with tin and hydrochloric acid. After separating the two benzoyl derivatives, it was found that the proportion of (B) to (A) is here approximately 12 to 1.

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LXXXVIII.—*Optically Active Derivatives of Phenylaminoacetic Acid.*

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THE semipinacolinic deamination of tertiary amino-alcohols has been applied by McKenzie, Roger, and Wills (J., 1926, 779) for the preparation of optically active ketones. It was desirable that optically active desylamine hydrochloride should be prepared in order that the behaviour of nitrous acid towards the amino-alcohols derived from it by means of Grignard reagents could be studied. This was one of the reasons why the present research was undertaken.

The resolution of *r*-desylamine gave unpromising results at first. The nicely-crystalline product from the interaction of *r*-desylamine hydrochloride and sodium hydrogen *d*-tartrate in aqueous solution did not lend itself to recrystallisation. Moreover, *d*-camphor-10-sulphonic acid and *d*-α-bromocamphorsulphonic acid also gave unsatisfactory results. It was thought possible that phthalyl derivatives of phenylaminoacetic acid might serve the purpose, and that *l*-α-phthalimidophenylacetyl chloride would give optically active desylamine hydrochloride through the intermediate stages of desylphthalimide and desylphthalamic acid:

$$NH_2\cdot CHPh\cdot CO_2H \longrightarrow C_8H_4O_2{:}N\cdot CHPh\cdot CO_2H \longrightarrow$$
$$C_8H_4O_2{:}N\cdot CHPh\cdot COCl \longrightarrow C_8H_4O_2{:}N\cdot CHPh\cdot COPh \longrightarrow$$
$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CHPh\cdot COPh \longrightarrow NH_2\cdot CHPh\cdot COPh,HCl.$$

The optically active α-phthalimidophenylacetic acid cannot be obtained by heating *l*-phenylaminoacetic acid with phthalic anhydride at 160—170°, presumably owing to the racemisation which occurs at this temperature. After preliminary experiments with various alkaloids, the resolution of the *r*-phthalyl acid was successfully accomplished by morphine. When, however, the acid chloride of the *l*-acid was acted on by benzene and aluminium chloride, the product was *r*-desylphthalimide.

l-α-Phthalimidophenylacetic acid, when hydrolysed with caustic soda under the conditions described in the experimental section, gave a dextrorotatory dicarboxylic acid with the probable constitution $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CHPh\cdot CO_2H$.

The next stage was to start with *r*-desylphthalamic acid. This was resolved by morphine, but we were not satisfied at the time that the desylamine hydrochloride obtained by hydrolysing the *l*-acid was optically pure, and subsequent experiments confirmed this view. The concentrated hydrochloric acid used in the hydrolysis was apparently the racemising agent. It was further found that *l*-desylphthalamic acid gives on dehydration *r*-desylphthalimide.

It remained, therefore, to revert to the resolution of *r*-desylamine itself. By the application of *l*-mandelic acid and *d*- and *l*-γγγ-trichloro-β-hydroxybutyric acids—substances which have not hitherto been used for the resolution of *r*-bases—the optically active desylamine hydrochlorides are now accessible in sufficient quantity to enable them to be applied for our studies on the migration of groups.

The *d*- and *l*-desylamines have a certain interest on account of their connexion with the *d*- and *l*-benzoins. When *d*-desylamine hydrochloride was acted on by nitrous acid, a mixture of *r*- and *d*-benzoins was formed, so that the following change was effected:

$$d\text{-Ph}\cdot\text{CH(NH}_2)\cdot\text{COPh,HCl} \xrightarrow{(\text{HNO}_2)} d\text{-Ph}\cdot\text{CH(OH)}\cdot\text{COPh}.$$

When the free base, which is very unstable, was liberated from the *d*-hydrochloride, the sign of rotation was unaltered. Its optical activity in ethyl-alcoholic solution was evanescent at the ordinary temperature, a result which we attribute—in part at least—to racemisation rather than to decomposition.

EXPERIMENTAL.

Action of Phthalic Anhydride on l-*Phenylaminoacetic Acid.*—2 G. of *l*-phenylaminoacetic acid were heated for 2½ hours with freshly-distilled phthalic anhydride (2 g.) at 160—170°. The product was crystallised first from glacial acetic acid and then from benzene. The resulting acid (3 g.) was optically inactive in acetone and in benzene: it consisted of *r*-α-phthalimidophenylacetic acid, m. p. 170·5—171·5° (Ulrich, *Ber.*, 1904, **37**, 1685).

This behaviour of optically active phenylaminoacetic acid, $C_6H_5\cdot CH(NH_2)\cdot CO_2H$, is in marked contrast with that of *d*-β-amino-β-phenylpropionic acid, $C_6H_5\cdot CH(NH_2)\cdot CH_2\cdot CO_2H$, from which *d*-β-phthalimido-β-phenylpropionic acid is readily prepared when the amino-acid is heated with phthalic anhydride (McKenzie and Tudhope, J., 1924, **125**, 928), no racemisation occurring in the latter case.

Resolution of r-α-*Phthalimidophenylacetic Acid.*—Morphine (30·7 g.) was dissolved by heating with ethyl alcohol (2850 c.c.), the solution cooled to 30°, and the *r*-acid (28·5 g.) added. The acid dissolved readily. The morphine salt (36·5 g.), which had separated over-

night, was crystallised once from ethyl alcohol (2900 c.c.), and the resulting needles were dissolved in boiling water (2500 c.c.), and decomposed, while the solution was still warm, by concentrated hydrochloric acid. The acid precipitated was crystallised once from aqueous acetone, washed with ice-cold water, and dried in a vacuum over sulphuric acid. It was then optically pure, repeated crystallisation failing to raise the value of its specific rotation. Yield: 10 g.

l-*α-Phthalimidophenylacetic acid*, $C_8H_4O_2{:}N{\cdot}CHPh{\cdot}CO_2H$, forms glassy needles, m. p. 192—193° (Found: C, 68·3; H, 4·0; N, 5·1. $C_{16}H_{11}O_4N$ requires C, 68·3; H, 3·9; N, 5·0%). In acetone: $l = 2$, $c = 3{\cdot}5385$, $\alpha_D^{14\cdot5^\circ}$ −3·67°, $[\alpha]_D^{14\cdot5^\circ}$ −51·9°. In methyl alcohol: $l = 2$, $c = 4{\cdot}588$, $\alpha_D^{17\cdot5^\circ}$ −1·86°, $[\alpha]_D^{17\cdot5^\circ}$ −20·3°; $l = 2$, $c = 2{\cdot}251$, $\alpha_{5461}^{12\cdot5^\circ}$ −1·11°, $[\alpha]_{5461}^{12\cdot5^\circ}$ −24·7°.

Conversion of l-*α-Phthalimidophenylacetic Acid into* r-*Desylphthalimide.*—The *l*-acid (3 g.) was heated on the water-bath with thionyl chloride (20 g.) for 3 hours, and the excess of thionyl chloride removed; the residual oil gradually crystallised when kept in a vacuum over soda-lime. This acid chloride was then heated for 3 hours with dry thiophen-free benzene (30 c.c.) and aluminium chloride (3 g.), and the product was decomposed by dilute sulphuric acid. The solid obtained from the benzene solution was crystallised from pyridine–ethyl alcohol, and the crystals obtained (1·5 g.) were identified as *r*-desylphthalimide.

The racemisation observed must have occurred during the Friedel and Crafts reaction, since the acid chloride is lævorotatory. The product obtained by heating the *l*-acid (1 g.) for 2 hours with thionyl chloride (5 g.) gave in benzene ($l = 2$, $c = 3{\cdot}33$), α_D −4·68°.

Action of Potassium Hydroxide on l-*α-Phthalimidophenylacetic Acid.*—The *l*-acid (3 g.) was neutralised at the ordinary temperature by dissolving it gradually in 247·4 c.c. of caustic potash ($N/10 \times 0{\cdot}863$). After 1 hour the solution was acidified by dilute hydrochloric acid, and the precipitated acid collected (m. p. 177—179°). It was *dextrorotatory*, its rotation in acetone ($l = 2$, $c = 1{\cdot}266$) being α_D + 2·25°, $[\alpha]_D$ + 88·9°. Yield: 2·4 g. After crystallisation from aqueous acetone, it gave in acetone ($l = 2$, $c = 1{\cdot}2525$), α_D + 2·55°, $[\alpha]_D$ + 101·8°. The compound was now apparently homogeneous because, after two further crystallisations from aqueous acetone, it was unaltered in its specific rotation. The amount of alkali (of the strength given above) required to form the potassium salt from 3 g. of *l*-α-phthalimidophenylacetic acid is 123·63 c.c., whereas the amount actually added was 247·4 c.c. The amount of alkali required to effect the change

$$C_6H_4{<}{}^{CO}_{CO}{>}N{\cdot}CHPh{\cdot}CO_2H \xrightarrow{2KOH} CO_2K{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CHPh{\cdot}CO_2K$$

is 247·26 c.c. It would therefore appear that the dextrorotatory dicarboxylic acid, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CHPh{\cdot}CO_2H$, was formed by hydrolysing *l*-α-phthalimidophenylacetic acid under the conditions quoted.

Resolution of r-*Desylphthalamic Acid*.—270 C.c. of water were added to a solution of a mixture of 27 g. of the *r*-acid (Neumann, *Ber.*, 1890, **23**, 995) and 22·7 g. of morphine in 270 c.c. of ethyl alcohol. After 3 hours at the ordinary temperature, crystallisation started on stirring. The glassy prisms (23·5 g.), which separated over-night, were crystallised twice from 50% aqueous alcohol. Yield: 12·2 g. After decomposition of the salt by dilute sulphuric acid, the acid was extracted with ether. Yield: 6·1 g. It was almost pure, giving in acetone ($l = 2$, $c = 2{\cdot}4965$), $\alpha_D^{18^\circ}$ $-7{\cdot}85^\circ$, $[\alpha]_D^{18^\circ}$ $-157{\cdot}2^\circ$. It was finally crystallised from ether.

l-*Desylphthalamic Acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CHPh{\cdot}COPh$, is sparingly soluble in water, benzene, and light petroleum. It separates from ether in feathery needles, m. p. 155—157° (decomp.). In acetone: $l = 2$, $c = 2{\cdot}545$, $\alpha_D^{15^\circ}$ $-8{\cdot}10^\circ$, $[\alpha]_D^{15^\circ}$ $-159{\cdot}1^\circ$.

l-Desylphthalamic acid underwent dehydration to *r*-desylphthalimide under the following conditions. A solution of 1·3 g. of the acid in acetone–water was evaporated to dryness on the water-bath, a bright yellow mixture of solid and oil being obtained. The solution in acetone was only slightly lævorotatory, and from it colourless crystals of *r*-desylphthalimide (0·6 g.) separated gradually.

Hydrolysis of l-*Desylphthalamic Acid*.—The *l*-acid (1·7 g.) was evaporated to dryness on the steam-bath with concentrated hydrochloric acid (50 c.c.), and the aqueous solution of the residual solid was extracted 4 times with ether. The aqueous solution was evaporated to dryness, and the resulting desylamine hydrochloride (1 g.) was examined polarimetrically in ethyl alcohol: $l = 2$, $c = 3{\cdot}4685$, α_D $-7{\cdot}52^\circ$, $[\alpha]_D$ $-108{\cdot}4^\circ$. After one crystallisation from a mixture of water (10 c.c.) and concentrated hydrochloric acid (25 c.c.), the value for $[\alpha]_D$ was increased to $-110{\cdot}3^\circ$ ($c = 2{\cdot}9765$), and after one crystallisation more from the same solvent, to -114° ($c = 3{\cdot}269$). From those values alone it was clear that some racemisation must have occurred during the formation of desylamine hydrochloride, the racemising agent presumably being the concentrated hydrochloric acid employed (compare Fitger, "Racemisierungserscheinungen bei optisch-aktiven Sulphidsäuren," Lund, 1924). It was also proved that the racemisation was pronounced: the mother-liquor, from which the crystals giving $[\alpha]_D$ -114° had been removed, was evaporated to dryness, and the desylamine hydrochloride obtained in this manner gave the following low value in ethyl alcohol: $l = 1$, $c = 1{\cdot}572$, α_D $-0{\cdot}57^\circ$, $[\alpha]_D$ $-36{\cdot}3^\circ$.

The action of concentrated hydrochloric acid on *l*-desylphthalamic acid was accordingly examined as follows. 0·5 G. of the *l*-acid was added to 25 c.c. of hydrochloric acid (*d* 1·2) and kept for 10 days in the ice-chest. The *l*-acid was practically undissolved, and the value for its specific rotation had not fallen after this treatment. On the other hand, the racemisation was very pronounced under the following conditions at the ordinary temperature. Dry hydrogen chloride was passed into a solution of the *l*-acid (0·7 g.) in ether (100 c.c.). There was no separation of desylamine hydrochloride, and 30 c.c. of hydrochloric acid (*d* 1·2) were added. After 4 days with occasional shaking, the lower layer was evaporated to dryness, and the resulting solid had the following rotation in ethyl alcohol: $l = 2$, $c = 1·62$, α_D $-2°$, $[\alpha]_D$ $-62°$. The ethereal layer was evaporated at the ordinary temperature and the desylphthalamic acid thus obtained exhibited only a slight lævorotation in acetone: $l = 2$, $c = 1·008$, α_D $-0·23°$, $[\alpha]_D$ $-11°$.

Resolution of r-*Desylamine Hydrochloride*.—(1) *Resolution with* l-*mandelic acid*. A solntion of 15 g. of *r*-desylamine hydrochloride (Pschorr and Brüggemann, *Ber.*, 1902, **35**, 2740) in 130 c.c. of water was mixed with 75 c.c. of an aqueous solution of ammonium *l*-mandelate prepared from 9 g. of *l*-mandelic acid. The voluminous, colourless precipitate was drained off, and dissolved in boiling rectified spirit; the solution became orange-red. On cooling, yellow needles separated. These, after being washed with rectified spirit, became colourless (7 g.) and gave in acetone, in which the salt is somewhat sparingly soluble at the ordinary temperature, ($l = 2$, $c = 2·076$), α_D $-2·38°$, $[\alpha]_D$ $-57·3°$. The solntion was yellow. The acetone was expelled by warming on the water-bath, the residue being an oil with the colour of port wine. The remainder of the mandelate was crystallised from rectified spirit; the crystals (3·8 g.) obtained had the following rotation in acetone: $l = 2$, $c = 1·426$, α_D $-1·64°$, $[\alpha]_D$ $-57·5°$. The salt was thus apparently homogeneous; it melted at 149—150° with decomposition to an orange-coloured solution. It was decomposed by dilute hydrochloric acid, the mandelic acid was removed completely by extraction with ether, and the aqueous layer containing the desylamine hydrochloride was evaporated to dryness. After one crystallisation from ethyl alcohol, the hydrochloride was optically pure.

d-*Desylamine hydrochloride*, $C_6H_5·CH(NH_2)·CO·C_6H_5,HCl$, is more soluble in ethyl alcohol than is the *r*-isomeride. It separates in glassy prisms, which decompose with rapid evolution of gas at 230° (Found: C, 67·9; H, 5·6; N, 5·8; Cl, 14·1. $C_{14}H_{14}ONCl$ requires C, 67·9; H, 5·7; N, 5·7; Cl, 14·3%). In ethyl alcohol: $l = 2$, $c = 2·538$, $\alpha_D^{18°}$ $+11·33°$, $[\alpha]_D^{18°}$ $+223·2°$.

(2) *Resolution with* l-$\gamma\gamma\gamma$-*trichloro*-β-*hydroxybutyric acid*. 52 G. of the *l*-chloro-acid (McKenzie and Plenderleith, J., 1923, **123**, 1090) were neutralised by ammonia, and added to an aqueous solution of *r*-desylamine hydrochloride (62 g.). The flocculent crystals, which separated quickly from the solution (1500 c.c.), were collected, and after drying over concentrated sulphuric acid were crystallised from 1 litre of rectified spirit, the solution assuming an orange-red tint. Over-night at about 8°, colourless needles (35 g.) had deposited. These were decomposed by dilute hydrochloric acid, and extracted with ether, the *l*-chloro-acid being recovered from the ethereal solution. The aqueous solution was then evaporated until crystallisation started. The desylamine hydrochloride (18 g.) which separated on cooling was almost optically pure. The pure *d*-desylamine hydrochloride was obtained after two crystallisations from ethyl alcohol.

(3) *Resolution with* d-$\gamma\gamma\gamma$-*trichloro*-β-*hydroxybutyric acid*. The l-*desylamine hydrochloride* obtained resembled the enantiomorphous form in crystalline appearance, melting point, and optical rotatory power. In each one of these resolutions, the desylamine hydrochloride obtained had the opposite sign of rotation from that of the optically active acid employed.

Action of Nitrous Acid on d-*Desylamine Hydrochloride*.—10 C.c. of hydrochloric acid (2*N*) were added to a solution of 1·4 g. of *d*-desylamine hydrochloride in 20 c.c. of water. A solution of 1·2 g. of sodium nitrite in 15 c.c. of water was then gradually added (15 mins.), the temperature being kept at 0°. After 5 hours at 0°, a further addition of sodium nitrite (0·6 g. in 10 c.c.) was made. Over-night in the ice-chest, a yellow, somewhat oily, solid (0·95 g.) was obtained which in ethyl alcohol gave: $l = 2$, $c = 1{\cdot}25$, $\alpha_D + 0{\cdot}76°$, $[\alpha]_D + 30{\cdot}4°$. The product was crystallised from ethyl alcohol, and the colourless, gritty crystals which separated were examined in ethyl alcohol: $l = 2$, $c = 1{\cdot}178$, $\alpha_D + 0{\cdot}71°$, $[\alpha]_D + 30{\cdot}1°$. This product was partly racemised *d*-benzoin. It melted indefinitely at 127—131°, and reduced Fehling's solution.

For comparison, *l*-benzoin, prepared from *l*-mandelamide and magnesium phenyl bromide (McKenzie and Wren, J., 1908, **93**, 309), was examined in ethyl-alcoholic solution: $l = 2$, $c = 1{\cdot}155$, $\alpha_D^{16°} -3{\cdot}06°$, $[\alpha]_D^{16°} -132{\cdot}5°$. There was, therefore, considerable racemisation in the displacement of the amino-group in *l*-desylamine hydrochloride.

d-*Desylamine*.—The instability of *r*-desylamine is clear from the work of Braun (*Ber.*, 1889, **22**, 557), Neumann (*loc. cit.*), and Pschorr and Brüggemann (*loc. cit.*). We confirmed the observations of the last-named authors, obtaining by crystallisation from ether a

colourless solid, m. p. 110° (decomp.). This specimen became yellow when kept. The *d*-base exhibits a similar instability.

18·5 C.c. of sodium carbonate ($N/2$) were added slowly with constant stirring to a solution of 2·5 g. of *d*-desylamine hydrochloride in 40 c.c. of water. The bulky, colourless precipitate was filtered off, washed three times with water, dried between filter-paper, and transferred to a desiccator, where it was kept over-night. The solid (1·5 g.) had now become bright yellow. It was found, however, to contain a small amount of the hydrochloride. To the filtrate from which this 1·5 g. had separated, and which had been kept over-night, 1·5 c.c. of sodium carbonate ($N/2$) were added. After ½ hour, the solid which had separated was collected, and dried over-night in a vacuum. It amounted to 0·4 g. and was colourless. It melted indefinitely at 82—86°, becoming bright yellow. 0·2504 G. was made up to 20 c.c. with ethyl alcohol and then gave α_D + 5·02° ($l = 2$), whence $[\alpha]_D$ + 200·5°. After 2 hours at the ordinary temperature, this value had fallen to + 4·20°; after 3 hours, the value was + 3·96°; after 21 hours, + 1·46°, and after 72 hours, + 0·28°. This drop in rotation was apparently mainly due to racemisation and not to decomposition, since, when an excess of hydrochloric acid was added to the solution giving α_D + 0·28° and the solution then evaporated to dryness, *r*-desylamine hydrochloride, m. p. 243—245° (decomp.), was obtained.

The *d*-base was liberated from *d*-desylamine hydrochloride (1·5 g.) in aqueous solution by the addition of caustic soda in slightly under the calculated amount. An oil was first deposited, and this solidified in a freezing mixture. It was washed twice with water, and dried over-night in a vacuum over sulphuric acid. The yellow product melted indefinitely, mainly between 87—89° with preliminary softening. Yield: 0·9 g. 0·2497 G. was made up to 20 c.c. with ethyl alcohol, and the rotation taken 5 minutes after the addition of the alcohol was begun. The progress of the racemisation is indicated by the following figures ($l = 2$):

Time (hours)	—	1	1½	2	3½
α_D	+4·60°	+4·50°	+4·40°	+4·27°	+3·94°
Time (hours)	4½	5½	7½	24	48
α_D	+3·75°	+3·60°	+3·34°	+1·76°	+0·62°

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LXXXIX.—*Density and Electrostriction of Dilute Manganese Salt Solutions.*

By Alan Newton Campbell.

It has been pointed out by Valson (*Compt. rend.*, 1870, **73**, 441) and by Bender (*Wied. Ann.*, 1883, **20**, 560) that the densities of salt solutions can be calculated with fair accuracy from the equation

$$d_\mu = d_{(\mu)\sigma} + \mu(m_a + m_b)$$

where d_μ is the density of a solution of the substance in question, containing μ equivs. per litre, $d_{(\mu)\sigma}$ the density of an ammonium chloride solution of the same normality and m_a and m_b are moduli for the ions of the salt in question. In this paper, the modulus for manganese is evaluated from three salts in dilute solution.

Valson also pointed out that the molecular solution volume of a substance is never equal to its molecular volume in the solid state, but always less. This contraction is designated "electrostriction," and attributed to a contraction of the solvent (Drude and Nernst, *Z. physikal. Chem.*, 1894, **15**, 79). According to Nernst and also Polowzow (*Z. physikal. Chem.*, 1911, **75**, 513), the electrostriction should increase with dilution to a practically constant value, and this is usually the case, as shown by Kohlrausch (*Wied. Ann.*, 1895, **56**, 185) and by Lamb and Lee (*J. Amer. Chem. Soc.*, 1913, **35**, 1667). The latter workers obtain one exceptional electrostriction curve, resembling to some extent that of manganese nitrate now described. Again, according to Baxter and Wallace (*ibid.*, 1916, **38**, 91), the electrostriction curves of the alkali halides are normal; they point out that "at least two important influences must be at work, one producing expansion, the other contraction," and the same conclusion is obvious from the graphs in this paper.

None of the above investigators draws attention to the fact that the value of the molecular volume in the solid state, which determines the electrostriction, has no absolute value: it is obviously much greater than the true, incompressible volume of the molecules. There must therefore be a contraction of the solid on dissolving, and only when this is allowed for is it possible to determine whether the solvent contracts or not. The expression $M(n^2 - 1)/d(n^2 + 2)$, where n is the refractive index for light of infinite wave-length, is supposed to represent the true molecular volume. The refractive indices of the dilute manganese salt solutions used were therefore determined, and hence, by the mixture rule, the molecular refractivities of the solid salts. From these figures the amended electrostriction was calculated.

EXPERIMENTAL.

The method used for the determination of density was that of Kohlrausch and Hallwachs (*Wied. Ann.*, 1894, **53**, 14). The density determinations given are each the mean of several differing only in the fifth decimal place; moreover, the results for very dilute solutions were checked on solutions made anew. The solutions investigated were in all cases 0·5, 0·3, 0·2, 0·1, 0·05, 0·02, 0·01 equivalent-normal. As the densities of ammonium chloride solutions had not previously been determined below 1·0*N*, it was first necessary to determine these, in order to deduce the modulus. The figures taken for the densities of the solid anhydrous manganese salts were: for the chloride, $d = 2{\cdot}977$ (Baxter and Hines, *J. Amer. Chem. Soc.*, 1906, **28**, 1574), whence its molecular volume in the solid state = 42·3 c.c.; for the sulphate, $d = 2{\cdot}954$ (Bassermann, "Dichtigkeitsmessungen," Heidelberg, 1873), whence its molecular volume = 51·3 c.c. The density of anhydrous manganese nitrate is not known, on account of the difficulty of obtaining it pure. An approximate calculation of the molecular volume was, however, made from the known density of the hexahydrate, assuming the water of crystallisation to have the density of ice. The value obtained was 39 c.c. Owing to this uncertainty, the refractive indices of the solid are not given.

The volumetric apparatus was standardised before use. The solutions were made up in the first place by weighing, and checked by analysis. Crystalline, hydrated A.R. salts were used.

The refractive indices were measured for the hydrogen C and F lines, a Zeiss–Pulfrich refractometer being used. Water at 20° was circulated through the apparatus, which was standardised with pure water.

It was shown by Bender (*Wied. Ann.*, 1890, **39**, 89) that the refractive indices of salt solutions can be calculated by means of an equation identical with that already given for densities. The standard of reference is potassium chloride solution, and moduli are deduced for ions other than $K^{\cdot}$ and Cl'. Here also, the refractivity moduli have been deduced and, as a necessary preliminary, the refractive indices of potassium chloride solutions determined. In the case of the manganese salt solutions, the refractivity modulus, the molecular refractivity $[R_L]$ of the anhydrous solid salt, and the molecular dispersion of the anhydrous solid salt were calculated for [t]he concentrations 0·5*N*, 0·3*N*, and 0·2*N*. The specific refractivity [o]f the anhydrous solid salt is obtained by means of the mixture [form]ula. Below the above strengths, an experimental error of 1′ [introdu]ces such variations into the derived magnitudes as to render

them ambiguous; for instance, with 0·1*N*-manganese chloride, it would cause an error of about 25% in the modulus, and a much greater error in the molecular dispersion. With the concentrations for which calculations have been made, the variations in the latter, though not great, are not believed to have any theoretical significance. The results have therefore been averaged. For the more dilute solutions, the refractive index only is given.

In the tables, the concentrations are given in equivs. per litre, $m_{\frac{1}{2}Mn}$ is the density modulus for manganese, and E.-S. is the electrostriction (in c.c.)

Results.

Densities of Dilute Ammonium Chloride Solutions.

Conc.	$d_{15°}^{15°}$.	Conc.	$d_{15°}^{15°}$.
0·5	1·00828	0·05	1·00095
0·3	1·00521	0·02	1·00033
0·2	1·00346	0·01	1·00019
0·1	1·00169	0·005	1·00009

Manganese Chloride Soltns. / *Manganese Sulphate Soltns.*

Conc.	$d_{15°}^{15°}$.	$m_{\frac{1}{2}Mn}\times 10^4$.	E.-S.	$d_{15°}^{15°}$.	$m_{\frac{1}{2}Mn}\times 10^4$.	E.-S.
0·5	1·02599	354	20·4	1·03654	365	46·5
0·3	1·01587	355	22·3	1·02217	365	48·1
0·2	1·01033	343·5	19·75	1·01493	374	49·6
0·1	1·00507	338	17·85	1·00733	364·5	46·9
0·05	1·00240	290	12·45	1·00366	342	46·7
0·02	1·00094	300·5	10·8	1·00142	345	42·3
0·01	1·00047	280	10·45	1·00071	320	42·0

Manganese Nitrate Solutions.

Conc.	$d_{15°}^{15°}$.	$m_{\frac{1}{2}Mn}\times 10^4$.	E.-S.
0·573718	1·03685	350	−11·5
0·344231	1·02226	346	−10·5
0·229395	1·01493	352	− 9·9
0·114744	1·00742	348	−10·0
0·057372	1·00367	325	−12·0
0·022940	1·00160	445	+ 7·0
0·011474	1·00085	425	+ 8·0

A few determinations of the densities of dilute manganese chloride, sulphate, and nitrate solutions have been made by Wagner (*Z. physikal. Chem.*, 1890, **5**, 31) and the agreement is satisfactory. Long (*Wied. Ann.*, 1880, **11**, 37) has determined the densities of more concentrated solutions, but his results appear to be untrustworthy.

Refractive Indices of Solutions at 20°.

	Potassium chloride.		Manganese chloride.		Manganese sulphate	
Conc.	n_C.	n_F.	n_C.	n_F.	n_C.	n_F.
0·5	1·33636	1·34239	1·33803	1·34415	1·33770	1·34378
0·3	1·33437	1·34044	1·33535	1·34148	1·33535	1·34141
0·2	1·33327	1·33918	1·33402	1·34014	1·33377	1·33992
0·1	1·33228	1·33822	1·33254	1·33858	1·33253	1·33866
0·05	1·33196	1·33785	1·33196	1·33793	1·33171	1·33770
0·02	1·33163	1·33756	1·33163	1·33757	1·33131	1·33731
0·01	1·33147	1·33742	1·33147	1·33742	1·33123	1·33723
0·005	1·33131	1·33727	—	—	—	—
Pure water	1·33113	1·33713	—	—	—	—

Manganese Chloride.

Equiv. norm.	Modulus ($\frac{1}{2}$Mn) × 10³,		$[R_L]_C$	$[R_L]_F$	
Conc.	C line.	F line.	for anhydrous salt.		$[R_L]_F - [R_L]_C$.
0·5	3·3	3·5	20·3	20·5	0·217
0·3	3·3	3·5	20·0	20·4	0·377
0·2	3·8	4·8	21·2	21·7	0·537
Means	3·5	3·9	20·5	20·9	0·377

From the mean values of the molecular refractivities, the refractive indices of solid anhydrous manganese chloride were calculated to be: $n_C = 1·96$, $n_F = 2·00$.

Manganese Sulphate.

	$[R_L]_C$	$[R_L]_F$	
Conc.	for anhydrous salt.		$[R_L]_F - [R_L]_C$.
0·5	16·4	16·6	0·151
0·3	16·4	16·7	0·406
0·2	15·3	16·1	0·783
Means	*16·0*	*16·5*	*0·447*

Hence, refractive indices of solid anhydrous manganese sulphate: $n_C = 1·54$, $n_F = 1·56$.

Manganese Nitrate.

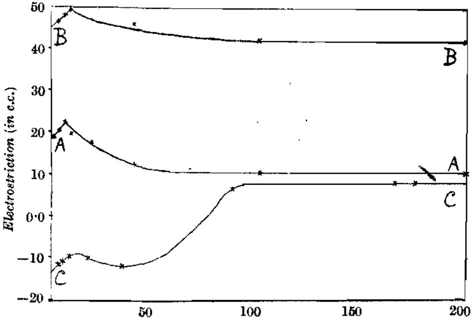
	$[R_L]_C$	$[R_L]_F$	
Conc.	for anhydrous salt.		$[R_L]_F - [R_L]_C$.
0·573718	24·8	25·5	0·657
0·344231	24·4	25·4	0·91
0·229395	24·5	25·8	1·54
Means	24·6	25·6	1·036

Jones and Getman (*Amer. Chem. J.*, 1904, **31**, 303) have determined the refractive indices, presumably for the sodium line, of manganese chloride, sulphate, and nitrate solutions; the figures they obtain for dilute solutions, however, are less than the refractive index of pure water, a state of affairs only possible with a concentrated solution of a substance of very low refractive index. Otherwise, their figures are concordant amongst themselves. It is suggested that their instrument was affected by a constant error.

The following table contains the electrostrictions, calculated on the assumption that the expression $M(n^2 - 1)/d(n^2 + 2)$ represents the true molecular volume of the salt.

$MnCl_2$.		$MnSO_4$.		$Mn(NO_3)_2$.	
Conc.	E.-S.	Conc.	E.-S.	Conc.	E.-S.
0·5	− 1·4	0·5	+11·2	0·573718	−25·9
0·3	+ 0·5	0·3	+12·8	0·344231	−24·9
0·2	− 2·1	0·2	+14·3	0·229395	−24·3
0·1	− 4·0	0·1	+11·6	0·114744	−24·4
0·05	− 9·4	0·05	+11·4	0·057372	−26·4
0·02	−11·0	0·02	+ 7·0	0·022940	− 7·4
0·01	−11·4	0·01	+ 6·7	0·011474	− 6·4

FIG. 1.



Dilution (litres per mol.).
A. Manganous chloride solutions.
B. " sulphate "
C. " nitrate "

Conclusion.

In the first place, it is obvious from the tables that the density modulus is fairly constant, except at very high dilutions, and therefore the density can be calculated down to $0{\cdot}1N$ by using the mean modulus of 355. In calculating the modulus from sulphate and nitrate solutions, it was necessary to employ the accepted moduli for $\frac{1}{2}SO_4$ and NO_3 (200 and 150, respectively).

The forms of the electrostriction curves are remarkable. Exactly the same forms of curves are given by Wagner's figures (*loc. cit.*). Presumably the maxima indicate, as suggested by Baxter and Wallace (*loc. cit.*), the existence of two opposing processes, one

preponderating on each side of the maximum. The forms of the curves are of course independent of the values assigned to the densities and molecular volumes of the anhydrous solid salts.

It would appear from the last table that the effect of calculating with the "true molecular volume" is to indicate, in the cases of manganese chloride and manganese nitrate solutions, a negative electrostriction, *i.e.*, an expansion of the solvent.

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XC.—*Equilibrium between Alcohols and Salts. Part II.*

By ELLIS LLOYD, CONRAD BEVAN BROWN, DAVID GLYNWYN ROBERT BONNELL, and WILLIAM JACOB JONES.

INVESTIGATION has been continued on the lines already described (J., 1926, 318, 321). The compositions of the solid phases have also been investigated by Bagster's method (J., 1917, **111**, 494).

The density, without correction of the weighings to vacuum, of the methyl alcohol used was $d_{4^\circ}^{25^\circ}$ 0·78661, and that of the ethyl alcohol 0·78505. In the case of the higher aliphatic alcohols, the purest commercial product was first fractionally distilled and then further purified by the method employed by Orton and Jones (J., 1919, **115**, 1194) for *n*-butyl alcohol. The alcohol thus purified was dried, first by standing over anhydrous potassium carbonate, and then by refluxing over calcium turnings until further boiling effected no change in the density of a sample distilled off, whereupon the distillate was accepted for use. The boiling points at 760 mm. and densities ($d_{4^\circ}^{25^\circ}$) were : *n*-propyl alcohol, 97·3°, 0·79970; *n*-butyl alcohol, 117·7°, 0·80569; *n*-amyl alcohol, 137·2°, 0·80942; *iso*amyl alcohol, 130·8°, 0·80484. The benzyl alcohol, purified by fractional distillation under reduced pressure, had $d_{4^\circ}^{25^\circ}$ 1·0402.

The salts were purified by the method previously described, with the exception of the magnesium chloride and nitrate, both of which were prepared in the form of their alcoholates by crystallisation from the filtered alcoholic extracts of the ignited salts, the whole preparation being conducted in a closed apparatus out of contact with the air. The degree of purity of the salts was : $CoCl_2$, $HgBr_2$, each 99·4%; CaI_2, 99·6%; $CdBr_2$, CdI_2, $CuCl_2$, $NiBr_2$, each 99·8%; $LiCl$, $CaCl_2$, $CaBr_2$, $SrBr_2$, $BaBr_2$, $Ba(NO_3)_2$, $MgCl_2,6CH_3{\cdot}OH$, $MgCl_2,6C_2H_5{\cdot}OH$, $CdCl_2$, $CoBr_2$, $FeCl_3$, each 99·9%; NaBr, NaI, KBr, $Mg(NO_3)_2,6CH_3{\cdot}OH$, $Mg(NO_3)_2,6C_2H_5{\cdot}OH$, $Ca(NO_3)_2$, $HgCl_2$, $NiCl_2$, $AlCl_3$, each 100·0%.

Determinations of solubility in methyl alcohol over ranges of temperature have been carried out by Menschutkin (*Z. anorg. Chem.*, 1907, **52**, 9) on calcium chloride, magnesium bromide, and nagnesium iodide; by Étard (*Compt. rend.*, 1892, **114**, 112; *Ann. Chim. Phys.*, 1894, **2**, 555) on mercuric and cupric chlorides; by Lemoine (*Compt. rend.*, 1897, **125**, 604) on lithium chloride; and by Centnerszwer (*Z. physikal. Chem.*, 1910, **72**, 431) and Tyrer J., 1910, **97**, 621) on potassium iodide.

The solubilities of strontium bromide and of sodium iodide in thyl alcohol have been determined, respectively, by Fonzes-Diacon J. *Pharm. Chim.*, 1895, **1**, 59) and by King and Partington (J., 926, 20).

The higher alcoholates have been but little investigated. Étard *loc. cit.*) measured the solubilities of mercuric and cupric chlorides n *n*-propyl, *iso*propyl, *iso*butyl, amyl, and allyl alcohols. Menchutkin (*loc. cit.*) prepared the hexa-alcoholates of magnesium romide and iodide with *n*-propyl, *iso*butyl, and *iso*amyl alcohols, nd he also investigated the solubility of the bromide in these lcohols. Loeb (*J. Amer. Chem. Soc.*, 1905, **27**, 1019) described a odium iodide *n*-propyl alcoholate. Turner and Bissett (J., 1913, 03, 1904; 1914, **105**, 1783) prepared the tetra-alcoholates of the ithium halides with various higher alcohols, and made determintions of the solubilities of the alkali halides at 25°.

As regards solvent power for salts, methyl alcohol was placed ntermediate between water and ethyl alcohol by Dumas and Péligot (*Ann. Chim. Phys.*, 1835, **58**, 18), whilst von Weimarn J. *Russ. Phys. Chem. Soc.*, 1908, **40**, 1126) placed the alcohols in he order: methyl, ethyl, propyl, butyl, and amyl. These rules, owever, are liable to exceptions; *e.g.*, the greater solubility of alcium chloride and bromide in *n*-butyl alcohol than in *n*-propyl lcohol.

In the calculation of dissociation pressure in the gas-current nethod adopted in the present investigation, Dalton's law is assumed o hold for a mixture of air and alcohol vapour at pressures of lcohol which are below the saturation point. In order to see ow far the alcohol vapour in the mixtures deviates from the ideal, we have compared the value of pv (p denoting the pressure of lcohol in mm. of mercury, and v its molecular volume in c.c.) iven by the ideal-gas equation with that given by the van der Vaals equation, which, despite molecular association on the part f the alcohol, gives the order of magnitude of the deviation. Thus, ven in the experiment in which the deviation is greatest, for a ressure of methyl alcohol of 95·2 mm. at 60°, the value of pv iven by the ideal-gas equation is $2{\cdot}0773 \times 10^7$, whilst that given

by $(p + 7{\cdot}224 \times 10^9/v^2)(v - 66{\cdot}91) = 62{,}364T$, the van der Waals equation for methyl alcohol, is $2{\cdot}0747 \times 10^7$, an agreement which justifies the application of Dalton's law. Further, it is assumed that the vapour which passes over in the current of air is the alcohol itself, and not one of its products of decomposition. This point was tested by condensing the alcohol carried away from an ethyl-alcoholate by the passage of dry air under the conditions of the experiments. The condensed alcohol was found to be free from ether and water, and to contain only a negligible trace of aldehyde. The influence of total pressure on the dissociation pressure in the present experiments can be safely ignored. In the following tables, each value of a dissociation pressure given is the mean of several determinations.

The maximum work, A, obtainable by the isothermal vaporisation of a liquid to give 1 g.-mol. of a vapour which conforms with the van der Waals equation, followed by the expansion of the vapour to the dissociation pressure in a univariant system with two solid phases and by the combination of the vapour with one of the solids in the system, is given by the equation

$$A = RT \log_e \frac{V - b}{v - b} + \frac{RTb(V - v)}{(V - b)(v - b)} - \frac{2a(V - v)}{vV} - Pv' - \frac{p(v_1 - v_2)}{n}.$$

Here v denotes the molecular volume of the vapour in equilibrium with the liquid, V that of the vapour in equilibrium with the two solid phases, a and b the constants in the van der Waals equation, P the saturated vapour pressure, p the dissociation pressure, n the number of g.-mols. of the vapour which combine with one formula-weight (in grams) of the solid to give the addition compound, and v', v_1, and v_2 the volumes occupied by the formula-weight (in grams) of the liquid, reacting solid, and solid addition compound, respectively. Thus, for the dissociation of magnesium nitrate hexa-methyl-alcoholate at 60°, the value of the pressure, 95·2 mm., *on being substituted in the van der Waals equation gives* $V =$ 217,927 c.c., and the vapour pressure of methyl alcohol, 624·3 mm., gives 32,992 c.c., the value of n is 6, and the volumes of the condensed phases are $v' = 41$, $v_1 = 66$, and $v_2 = 274$; whence A is calculated by the above equation to be $3{\cdot}8896 \times 10^7$ (mm. of mercury) × (c.c.), or 1240·0 cals. If terms of low magnitude be ignored, the loss of free energy per g.-mol. of vapour on formation of the addition compound is given by $RT \log_e (P/p)$. In the case of the above example this expression has the value 1245·5 cals.

The variation of the dissociation pressure of an alcoholate with

temperature is, in general, such that over a moderate range the logarithm of the pressure is sensibly a rectilinear function of the reciprocal of the absolute temperature. Thus for magnesium nitrate hexa-methyl-alcoholate, the equation $\log_{10} p = 11{\cdot}02341 - 3006{\cdot}63/T$ gives at 30°, 40°, and 50° the pressures 12·7, 26·3, and 52·2 mm., respectively, whilst the direct determinations from the results of which the equation has been calculated give the respective values, 12·7, 26·3, and 52·3 mm. This form of variation is consequent on the fact that, when the heat of dissociation is great in comparison with the molecular heats of the substances involved, it is practically independent of temperature. If Q denote this heat per g.-mol. of alcohol vapour, and if it be assumed constant, integration of Clapeyron's equation gives the relation $\log_e p = I - Q/RT$, wherein I is the constant of integration. Thus for the given example, Q, which may be assumed to be the true heat of dissociation at the middle temperature, 40°, of the range, has the value 13,766 cals.

Between alcohols and salts there occur in many cases more profound reactions than solvation, ionisation, and alcoholysis. Such reactions are marked by their difficultly reversible character, and they often result in decomposition of both salt and alcohol. Thus, aluminium chloride when added to either methyl or ethyl alcohol gives an immediate violent evolution of hydrogen chloride. Ferric chloride does not react so vigorously, but its saturated solutions in both alcohols on standing at temperatures above 50° yield chloroform and deposit a red ferric precipitate, whilst they evolve hydrogen chloride on boiling. Below 50° the solubility of ferric chloride in these alcohols can be determined, although there is evidence of the slow formation of ethyl chloride in the ethyl-alcoholic solution. Even cupric chloride, when its saturated solution in ethyl alcohol is boiled, yields traces of chloroform.

EXPERIMENTAL.

Results.

In the following tables solubility is given as g. of salt per g. of alcohol, and pressure as mm. of mercury.

Solubility in methyl alcohol.

Temp.	LiCl.	NaBr.	KBr.	$CuCl_2$.	$BaBr_2$.	$Ba(NO_3)_2$.	CaI_2.
0°	0·452	0·173	0·0182	0·565	0·444	0·00070	1·164
10	0·442	0·170	0·0193	0·574	0·431	0·00065	1·211
15	0·440	0·169	0·0200	—	0·425	—	1·237
20	0·438	0·168	0·0208	0·586	0·419	0·00057	1·261
30	0·438	0·165	0·0223	0·600	0·409	0·00052	1·312
40	0·441	0·161	0·0237	0·618	0·402	0·00048	1·368
50	0·444	0·158	0·0255	0·644	0·394	0·00042	1·422
60	0·446	0·153	0·0274	0·664	0·388	0·00040	1·488

Temp.	$CaBr_2$.	$MgCl_2$.	$Mg(NO_3)_2$.	$CdCl_2$.	$CdBr_2$.	CdI_2.	$NiBr_2$.
0°	0·504	0·155	—	—	0·099	—	—
10	0·520	0·157	0·157	—	—	2·068	0·330
15	0·536	—	—	—	0·135	—	—
20	0·562	0·160	0·173	0·0215	0·162	2·067	0·351
25	—	—	—	—	0·184	—	—
30	0·629	0·167	0·209	0·0266	0·211	2·067	0·381
40	0·719	0·178	0·233	0·0344	0·245	2·060	0·433
50	0·832	0·190	0·269	0·0444	0·310	2·081	0·491
60	0·978	0·204	0·350	—	0·439	2·086	0·537
65	1·056	—	—	—	—	—	—
70	—	—	—	—	—	2·120	0·596

Temp.	NaI.	$Ca(NO_3)_2$.	$SrBr_2$.	$HgBr_2$.	$CoCl_2$.	$CoBr_2$.
10°	0·650	1·341	1·150	0·535	—	—
20	0·720	—	1·194	0·653	0·385	0·430
22	—	—	—	0·703	—	—
25	0·780	—	—	—	0·436	—
27	0·813	—	—	0·716	—	—
28	0·818	—	—	—	0·465	—
30	0·814	—	1·234	0·721	0·488	0·586
35	—	—	—	—	0·555	0·800
37	—	—	—	—	0·589	0·943
38	—	—	—	—	0·588	—
40	0·807	1·442	1·255	0·760	0·582	1·248
50	0·801	—	1·296	0·819	0·589	1·419
60	0·794	1·580	1·361	0·851	—	1·531
70	—	1·685	1·446	—	—	1·690
72	—	1·707	—	—	—	—
73	—	1·711	—	—	—	—
80	—	1·693	—	—	—	1·906

The solubility of ferric chloride in methyl alcohol is 1·31 at 0°, 1·43 at 15°, and 1·61 at 30°. These figures, however, should be accepted with reserve (see p. 661).

The following solubilities in methyl alcohol have been recorded : lithium chloride at 1°, 0·055 ; at 23°, 0·170 (Lemoine, *loc. cit.*) ; at 25°, 0·4236 (Turner and Bissett, *loc. cit.*) : sodium bromide at 18·5°, 0·170 (Lobry de Bruyn, *Z. physikal. Chem.*, 1892, **10**, 782) : potassium bromide at 25°, 0·0151 (Lobry de Bruyn), 0·0217 (Turner and Bissett) : cadmium chloride at 25°, 0·0171 (Lobry de Bruyn) : cadmium iodide at 20°, 2·20 (Timofejeff, *Compt. rend.*, 1891, **112**, 1224) : sodium iodide at 22·5°, 0·777 (Lobry de Bruyn); at 25°, 0·913 (Herz and Kuhn, *Z. anorg. Chem.*, 1908, **60**, 154), 0·9035 (Turner and Bissett).

Dissociation pressures of methyl-alcoholates (A denotes $CH_3·OH$).

	10°.	15°.	20°.	25°.	30°.	40°.	50°.	60°.
$CuCl_2$,2A	36·0	50·7	68·0	—	—	—	—	—
$MgCl_2$,6A	34·4	48·6	—	—	—	—	—	—
$Mg(NO_3)_2$,6A	—	—	5·6	—	12·7	26·3	52·3	95·2
$CdCl_2$,3A	—	—	93·5	—	—	—	—	—
$CdBr_2$,3A	52·2	—	—	—	—	—	—	—
$NiBr_2$,6A	8·5	—	17·4	—	34·8	68·9	—	—
NaI,3A	18·8	27·5	38·7	—	—	—	—	—
$Ca(NO_3)_2$,2A	—	11·4	15·2	—	29·4	52·4	74·0†	—
$SrBr_2$,1½A	12·8	18·3	24·7	—	43·9	—	—	—
$HgCl_2$,A	—	44·7	59·2	87·6	—	—	—	—
$HgBr_2$,A	52·0	—	—	—	—	—	—	—
$CoCl_2$,3A	—	—	29·4	40·9	59·0	81·9*	—	—
$CoBr_2$,6A	14·4	—	31·0	—	64·1	—	—	—

* At 35°. † At 45°.

In the following table and in the corresponding table relating to the ethyl alcoholates are given (1) the compositions of the solid phases, the successive stages of de-alcoholation being indicated, (2) the dissociation pressures at 20° measured by the static method of Bagster (*loc. cit.*), and (3) the transition points. The solid phase in equilibrium with the saturated solution at 20° is in each case marked with an asterisk. In the case of each salt the alcoholate given last in the column headed " Solid phase " is the lowest, and on dissociation yields the non-alcoholated salt, *e.g.*, $Mg(NO_3)_2,6CH_3{\cdot}OH$ on further withdrawal of alcohol yields $Mg(NO_3)_2$ directly. Results of analysis are given only where the alcoholates are described for the first time.

Methyl-alcoholates.

Solid phase.	Salt in solid phase, %. Found.	Calc.	Dissoc. press. in mm. at 20°.	Transition point.
$LiCl,3CH_3{\cdot}OH$	—	—	—	0·1°
*$CuCl_2,2CH_3{\cdot}OH$	65·0	67·7	—	—
*$CaI_2,6CH_3{\cdot}OH$	60·3	60·5	47	—
$CaI_2,2CH_3{\cdot}OH$	81·2	82·1	20	—
*$Mg(NO_3)_2,6CH_3{\cdot}OH$	46·9	43·6	—	—
*$CdCl_2,3CH_3{\cdot}OH$	64·9	65·6	94	21·8
$CdCl_2,2CH_3{\cdot}OH$	74·3	74·1	29	—
$CdCl_2,1\frac{1}{2}CH_3{\cdot}OH$	79·4	79·2	19	—
*$CdBr_2,3CH_3{\cdot}OH$	74·5	74·0	94	29·0
$CdBr_2,2CH_3{\cdot}OH$	80·8	80·9	26	—
$CdBr_2,1\frac{1}{2}CH_3{\cdot}OH$	84·5	85·0	15	—
*$NiBr_2,6CH_3{\cdot}OH$	53·0	53·2	17	48
*$NaI,3CH_3{\cdot}OH$	60·3	60·9	—	27·4
*$Ca(NO_3)_2,2CH_3{\cdot}OH$	71·6	71·9	—	72·2
*$SrBr_2,1\frac{1}{2}CH_3{\cdot}OH$	84·1	83·7	25	45·7
$SrBr_2,\frac{1}{2}CH_3{\cdot}OH$	94·2	93·9	11	—
*$HgCl_2,CH_3{\cdot}OH$	89·7	89·5	55	—
*$HgBr_2,CH_3{\cdot}OH$	93·4	91·8	74	22
*$CoCl_2,3CH_3{\cdot}OH$	57·3	57·5	30	37·1
$CoCl_2,2CH_3{\cdot}OH$	66·9	67·0	15	—
*$CoBr_2,6CH_3{\cdot}OH$	53·6	53·2	31	40
$CoBr_2,3CH_3{\cdot}OH$	69·5	69·5	17	—
$CoBr_2,2CH_3{\cdot}OH$	78·0	77·4	10	—

Throughout the investigated ranges of temperature, sodium bromide, potassium bromide, barium bromide, barium nitrate, and cadmium iodide exist in equilibrium with their respective saturated solutions as the non-alcoholated salts. So also does lithium chloride above 0·1°. In the case of magnesinm chloride, the solid phase consists of $MgCl_2,6CH_3{\cdot}OH$, which dissociates directly into $MgCl_2$. Calcium bromide in contact with the alcohol gives the tetra-alcoholate, the dissociation of which has already been investigated (J., 1926, 326). The tri-alcoholate of cobalt chloride is coloured amethyst, and the di-alcoholate a light purple-pink. The hexa-alcoholate of cobalt bromide forms reddish hexagonal columns, the tri-alcoholate is light blue, whilst the di-alcoholate is pale pink.

Solubility in ethyl alcohol.

Temp.	$CuCl_2$.	$MgCl_2$.	$Mg(NO_3)_2$.	$CdCl_2$.	$HgBr_2$.	$CoCl_2$.
0°	0·423	0·0361	0·0147	—	0·273	0·450
10	0·460	0·0434	—	0·0130	0·282	0·486
20	0·500	0·0560	0·0307	0·0148	0·286	0·544
30	0·541	0·0740	0·0539	0·0166	0·316	0·626
40	0·583	0·1000	0·1086	0·0191	0·340	0·674
50	0·639	0·1280	0·1653	0·0228	0·362	0·651
60	0·708	0·1589	0·2423	0·0278	0·423	0·668
65	—	0·1720	—	0·0286	—	—
70	—	0·1863	0·3402	0·0253	0·463	0·729
80	—	—	0·3263	—	—	0·703

Temp.	$Ca(NO_3)_2$.	$SrBr_2$.	$CdBr_2$.	CdI_2.	$CoBr_2$.
10°	0·462	0·636	0·269	—	0·706
20	0·514	0·639	0·300	1·105	0·771
30	0·562	0·649	0·335	1·081	0·849
40	0·629	0·735	0·378	1·038	0·959
45	—	—	0·393	—	—
50	0·735	0·752	0·381	1·027	1·050
60	0·821	0·755	0·303	1·033	1·208
70	0·901	0·757	0·223	1·034	1·271
80	0·918	0·778	—	1·037	1·294

In the case of ferric chloride and ethyl alcohol, a retroflex regio is encountered, the solid phases consisting of $FeCl_3,2C_2H_5{\cdot}OH$ an $FeCl_3$. The congruent melting point of the di-alcoholate is 50° The eutectic point for $FeCl_3$ and the di-alcoholate is 20·6°. Th di-alcoholate crystallises in flat prisms. Details regarding thi region are given in the following table.

	Solubility (g. $FeCl_3$ per g. of $C_2H_5{\cdot}OH$) and solid phase.		
Temp.	$FeCl_3$.	$FeCl_3,2C_2H_5{\cdot}OH$.	$FeCl_3,2C_2H_5{\cdot}OH$.
0°	—	—	1·36
15	—	—	1·41
20·6	*1·90	*1·90	*1·44
30	2·03	*1·94	*1·49
40	2·07	*1·87	*1·55
50	—	*1·76	*1·76

* The values thus marked were obtained by thermal analysis, the remainin values being determined by direct analysis. These results are somewha imprecise (see p. 661).

Previously recorded solubilities are : cobalt chloride at 13°, 0·5 (Bourion, *Compt. rend.*, 1902, **134**, 555, who describes the soli phase as $2CoCl_2,5C_2H_5{\cdot}OH$) : cadmium chloride at 15·5°, 0·015 (Lobry de Bruyn, *loc. cit.*); at 20°, 0·0391 (Jahn, *Ann. Physik* 1891, **43**, 296) : cadmium bromide at 20°, 0·349 (Jahn) : cadmiur iodide at 20°, 1·13 (Timofejeff, *loc. cit.*, who notes that no compoun formed) : strontium bromide, about 0·645 and nearly constan between 0° and 40° (Fonzes-Diacon, *loc. cit.*, who gives the formul alcoholate as $2SrBr_2,5C_2H_5{\cdot}OH$).

Dissociation pressures of ethyl-alcoholates (A denotes $C_2H_5{\cdot}OH$).

	10°.	20°.	25°.	30°.	35°.	40°.	50°
$CuCl_2$,2A	19·6	31·3	—	43·3	—	62·0	—
$MgCl_2$,6A	—	1·02	—	3·2	—	8·95	—
$Mg(NO_3)_2$,6A	2·4	6·2	9·7	14·5	22·5	32·3	—
$CdCl_2$,1½A	20·5	29·6	—	40·5	—	54·0	—
$CoCl_2$,3A	0·85	2·21	3·67	5·54	—	—	—
$Ca(NO_3)_2$,2A	—	13·8	—	27·8	—	55·3	—
$SrBr_2$,½A	8·0	15·2	—	—	—	—	—
$CdBr_2$,1½A	—	40·8	—	50·1	—	60·9	—
$CoBr_2$,3A	1·51	4·16	—	10·5	—	25·6	50·6

Ethyl-alcoholates.

Solid phase.	Salt in solid phase, %. Found.	Calc.	Dissoc. press. in mm. at 20°.	Transition point.
*$CuCl_2$,2A	57·1	59·4	—	—
*$Mg(NO_3)_2$,6A	—	—	6	67·5°
*$CdCl_2$,1½A	75·3	72·7	30	63·5
*$CdBr_2$,1½A	79·7	79·8	41	47·2
*$CoCl_2$,3A	48·4	48·5	2	38
$CoCl_2$,2A	57·9	58·5	1	—
*$CoBr_2$,3A	63·0	61·3	4	65
$CoBr_2$,2A	70·7	70·4	2	—
*$Ca(NO_3)_2$,2A	—	—	14	65·5
*$SrBr_2$,½A	92·3	91·5	14	40·5

Within the ranges of temperature investigated, neither cadmium iodide nor mercuric bromide is ethyl-alcoholated. In the case of magnesium chloride, the solid phase consists of the hexa-alcoholate, which on withdrawal of alcohol dissociates directly to $MgCl_2$. In the above table in the case of every salt the formula of the lowest alcoholate is given. The tri- and the di-ethyl-alcoholates of the chloride and bromide of cobalt are blue.

Solubility in higher alcohols.

Cupric chloride.

Alcohol.	10°.	20°.	30°.	40°.	50°.	60°.
n-Propyl ...	0·200	0·247	0·294	0·342	0·377	0·411
*iso*Amyl	0·107	0·121	0·142	0·166	0·210	0·252
Benzyl	0·0140	0·0165	0·0214	0·0302	0·0440	0·0612

Calcium chloride.

Alcohol.	0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.
n-Propyl ...	0·083	0·119	0·158	0·200	0·245	0·291	0·349	—
n-Butyl	0·162	0·214	0·257	0·291	0·316	0·335	0·348	—
n-Amyl	—	0·070	0·115	0·170	0·228	0·285	0·344	0·413
*iso*Amyl	—	0·030	0·072	0·121	0·170	0·228	0·269	0·316
Benzyl	—	0·0210	0·0182	0·0164	0·0145	0·0134	0·0125	—

Calcium bromide.

Alcohol.	0°.	10°.	20°.	30°.	40°.	50°.	60°.	70°.
n-Propyl ...	0·066	0·130	0·225	0·350	0·492	0·634	0·768	—
n-Butyl	0·183	0·253	0·339	0·437	0·543	0·648	0·752	—
n-Amyl	—	0·174	0·253	0·340	0·430	0·516	0·623	0·745
*iso*Amyl	—	0·217	0·256	0·299	0·369	0·434	0·500	0·562
Benzyl	—	0·129	0·150	0·170	0·177	0·174	0·172	0·170

Higher alcoholates.

In contact with the alcohol, cupric chloride forms green, needle-shaped crystals of the di-alcoholate, except with *n*-propyl alcohol, with which it forms no alcoholate under the conditions of the present experiments, whilst calcium chloride and bromide form tri-alcoholates ($CuCl_2,2iso\text{-}C_5H_{11}\cdot OH$: Found, $CuCl_2$, 42·2; calc., 43·3%. $CuCl_2,2C_6H_5\cdot CH_2\cdot OH$: Found, $CuCl_2$, 39·6; calc., 38·4%. $CaCl_2,3n\text{-}C_3H_7\cdot OH$: Found, $CaCl_2$, 36·1; calc., 38·0%. $CaCl_2,3n\text{-}C_4H_9\cdot OH$: Found, $CaCl_2$, 31·7; calc., 33·3%. $CaCl_2,3n\text{-}C_5H_{11}\cdot OH$: Found, $CaCl_2$, 27·0; calc., 29·5%. $CaCl_2,3iso\text{-}C_5H_{11}\cdot OH$: Found, $CaCl_2$, 27·0; calc., 29·5%. $CaCl_2,3C_6H_5\cdot CH_2\cdot OH$: Found, $CaCl_2$, 24·9; calc., 25·5%. $CaBr_2,3n\text{-}C_3H_7\cdot OH$: Found, $CaBr_2$, 50·8; calc., 52·6%. $CaBr_2,3n\text{-}C_4H_9\cdot OH$: Found, $CaBr_2$, 45·1; calc., 47·4%. $CaBr_2,3n\text{-}C_5H_{11}\cdot OH$: Found, $CaBr_2$, 41·2; calc., 43·1%. $CaBr_2,3iso\text{-}C_5H_{11}\cdot OH$: Found, $CaBr_2$, 42·6; calc., 43·1%. $CaBr_2,3C_6H_5\cdot CH_2\cdot OH$: Found, $CaBr_2$, 37·9; calc., 38·2%). The dissociation pressures of these compounds (Part I, *loc. cit.*, p. 328) indicate that the alcoholates of calcium bromide are generally more stable than those of calcium chloride, but in contact with the saturated solution the benzyl-alcoholate of calcium bromide breaks down into its components at 32°.

We desire to record our indebtedness to the Chemical Society for a grant which partly defrayed the expenses incurred in this investigation.

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XCI.—*Studies of Dynamic Isomerism. Part XXVI Consecutive Changes in the Mutarotation of Galactose.*

By GILBERT FREEMAN SMITH and THOMAS MARTIN LOWRY.

IN a paper on the "Dynamic Isomerism of the Reducing Sugars, recently contributed by one of us (*Z. physikal. Chem.*, Cohen Fest band, p. 125), a detailed examination was made of the evidenc for the unimolecular character of the mutarotation curves for glucos The conclusion was reached that, even under the most diver conditions of catalysis, the mutarotation of glucose and of tetr methyl glucose conforms strictly to the unimolecular law, withi the limits of experimental error,* although transient perturbatio

* Inflected curves have been observed, however, on two occasions wh tarotation was initiated by the addition of a drop of dilute acid or alk solution of tetra-acetyl glucose in dry ethyl acetate.

during the initial stages of the action are not excluded by the experimental data there cited. The unimolecular character of the curves can, however, be reconciled with the existence of an indefinitely large proportion of an intermediate μ form of the sugar, provided that the velocity coefficients and optical rotations of the three forms are distributed symmetrically, since under these conditions the first stage of the transformation proceeds according to the unimolecular law, whilst the second stage (which would give rise to an inflected curve) is not accompanied by any marked change of rotatory power. The real existence of this hypothetical second stage was established by comparing the rate of change of rotatory power with the rate of increase of solubility of glucose in aqueous alcohol, since this comparison showed that the chemical changes last about twice as long as the mutarotation, and therefore continue for a period of several hours after the changes of rotatory power are complete.

In the analogous case of galactose it has been generally (but erroneously) assumed that the mutarotation also proceeds according to a unimolecular law. Evidence of the existence of consecutive chemical changes was found, however, by Riiber and his colleagues (*Ber.*, 1926, **59**, 2266; compare *Ber.*, 1922, **55**, 3136, 3142) in the fact that the dissolution of the α-sugar in water at 20° *gives rise to an expansion during the first 15 minutes, followed by a contraction*, which only becomes logarithmic after 50 minutes have elapsed. In the same way they found that the initial stages of mutarotation are accompanied by an *absorption of heat,* which lasts for about 13 minutes at 0°, whereas the later stages are accompanied by a *liberation of heat.* The mutarotation of α-galactose is therefore associated with two consecutive changes of structure, which give rise to energy changes and volume changes of opposite sign, as we should expect them to be if the intermediate μ-compound is related in a symmetrical manner to the stereoisomeric α- and β-sugars. No analogous indications of the complexity of the process were obtained, however, from their observations of mutarotation, which appeared to be accurately unimolecular.

Anomalies in the Mutarotation of α-Galactose.—The present paper originated in an attempt to establish a standard value for the velocity coefficient of galactose, as had already been done in the case of glucose (J., 1927, 1736), as a preliminary to the determination of a catalytic catenary for the sugar. We found, however, that our mutarotation curves made no approach to the unimolecular law, since the velocity coefficient fell progressively from k_e = about 0·025 at 7 minutes to a limiting value of about 0·019. A survey of the literature confirmed the view that the mutarotation of galactose is not a simple unimolecular change. Thus, two of Urech's early experiments (*Ber.*, 1885, **18**, 3047) gave velocity

coefficients ranging irregularly from 0·0092 to 0·0153 and from 0·0071 to 0·0122, but the third showed a progressive decrease from 0·0132 to 0·0048 in the course of 11 hours at 14°. Since this decrease was attributed to a secondary transformation of the sugar (similar to that which results from the action of alkalis; compare Lobry de Bruyn, *Rec. trav. chim.*, 1895, **14**, 201), Urech's observations were cited by Riiber and Minsaas, together with the more exact investigation of Osaka (*Z. physikal. Chem.*, 1900, **35**, 668), as evidence that the mutarotation of galactose "proceeds according to the simple logarithmic equation of a reaction of the first order." Osaka's conclusion, "that the course of the alterations of rotatory power of the sugars, on which observations have been made, can be expressed by the velocity-formula for a reaction of the first order," appears to have been justified for most of the eight sugars for which data had been given by Tollens and his colleagues (*Annalen*, 1890, **257**, 164; 1892, **271**, 60); but an inspection of the tables shows that his velocity coefficient for galactose decreased progressively from 0·0120 to 0·0088 at $c = 10{\cdot}20$ and from 0·0131 to 0·0076 at $c = 11{\cdot}08$; his average value was therefore derived from numbers which show a systematic variation of from 50 to 80% from the limiting value. In the same way, we found that the average value, $k = 0{\cdot}00479$ (logarithms to base 10), given by Mackenzie and Ghosh (*Proc. Roy. Soc. Edin.*, 1914, **35**, 22) for the velocity coefficient of a 2·175% solution of galactose at 12·5°, was based on data which showed a progressive decrease from $k = 0{\cdot}0080$ at 8 minutes to $k = 0{\cdot}0036$ at 166—323 minutes. The data of Riiber and Minsaas, on the other hand, gave steady values for the velocity coefficient of α-galactose; but, since their first value was based on readings taken 20 and 30 minutes after dissolution, it is not surprising that they should have overlooked an anomaly which is really conspicuous only during the first 10 minutes.

Although the earlier data thus confirmed unanimously the large deviations from the unimolecular formula which we had observed in the mutarotation of α-galactose, we took the precaution of repeating the observations with specially purified samples of the sugar, which was recrystallised for this purpose from acetic acid and from alcohol according to a method for which we are indebted to Professor Haworth; similar results were also obtained when the polarimeter tube was kept at 0·2°. Finally, since the velocity coefficients covered just the same range of values at concentrations of 2½, 5, 10, and 15 g. of galactose in 100 c.c. of solution, it was clear that the action could not be multimolecular; we therefore concluded that the mutarotation was probably of a type which could be expressed by means of an equation involving two or more consecutive unimolecular changes.

Anomalies in the Mutarotation of β-Galactose.—Although Rüber and Minsaas recorded a steady value for the velocity coefficient of β-galactose from 10—20 minutes and onwards, Hudson and Yanovsky (*J. Amer. Chem. Soc.*, 1917, **39**, 1022) had already observed the anomaly of a *minimum* rotation in a solution of α- and β-galactose in water, which had been diluted with alcohol to a concentration of 60%. We therefore made a fresh study of the mutarotation of β-galactose in order to see whether the anomaly which we had observed in α-galactose could be detected when mutarotation took place in the reverse direction. Our first sample, prepared by the method of Hudson and Yanovsky, gave $[\alpha]_{5461} = 66°$, whilst the second and third samples both gave $[\alpha]_{5461} = 63{\cdot}5°$, no further reduction of rotatory power being produced when the second sample was washed four times more with 80% alcohol. A rough estimate of the rotatory dispersion of galactose showed that Hudson's value for the β-sugar $[\alpha]_D = 52°$ would correspond with a specific rotation $[\alpha]_{5461} =$ about 61°. This rotation is 2° less than our minimum, but, if deduced by extrapolation to zero time, would be appreciably too low, in view of the slowness with which mutarotation takes place during the first few minutes. We therefore think it probable that our sample was substantially pure, and suggest that an initial rotation $[\alpha]_{5461} = 63{\cdot}5°$ may be accepted as a provisional standard. This rotatory power remained constant, within the limits of experimental error, during a period of about 4 minutes; the rotation then increased rapidly, giving rise to an inflected mutarotation curve, with a maximum slope at about 10 minutes. The velocity coefficient, on the other hand, increased progressively from zero to a limiting value which was identical with that finally reached by the α-sugar.

Analysis of the Mutarotation Curves.—The view that "the interconversion of α- and β-glucose depends on the splitting of the oxide ring" and that "the aldehydic form of the sugar or its hydrate . . . is a necessary intermediate product in the conversion of α- into β-glucose or *vice versa*" (J., 1904, **85**, 1565) implies that the mutarotation of the α- or β-form of a reducing sugar depends on *two* consecutive unimolecular changes, as set out in the scheme

$$\underset{\alpha}{x} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\mu}{y} \underset{k_4}{\overset{k_3}{\leftrightharpoons}} \underset{\beta}{z}$$

Equations for an action of this type were therefore worked out at the request of one of us by Mr. H. Klugh in 1903, and a more complete analysis, in collaboration with Mr. W. T. John, was published in 1910 (J., **97**, 2634); but the only inflected mutarotation curves that have been studied hitherto (Lowry and Glover, J., 1913, **103**,

913) were too complex to be expressed by the preceding scheme; the data now recorded therefore provide the first opportunity that has arisen of completing this mathematical analysis.

Before giving an account of this investigation, however, we wish to make it clear that we are more concerned to demonstrate the *process* by which the analysis has been carried out than to attach a precise physico-chemical meaning to the *results* to which it leads, since these can only be regarded as valid when the fundamental assumptions on which the formulæ depend have been verified. In particular, the values deduced for the equilibrium concentration, y_∞, and the rotatory power, μ, of the intermediate sugar, depend on the hypothesis that only three sugars are concerned in the final equilibrium, *viz.*, the α- and β-sugars (6-ring oxides) and the intermediate (open-chain) μ-sugar, whereas we should prefer to postulate also the presence of a pair of γ-sugars (or 5-ring oxides), making 5 sugars in all. Whilst, therefore, our data can be represented completely by the empirical equations for 3 isomerides, we do not regard this as a proof that only *three* sugars are present in the final equilibrium, since we should then be obliged to admit the unimolecular form of the mutarotation curves of α- and β-glucose as evidence that only *two* isomerides are formed in an aqueous solution of glucose. Again, since a mathematical analysis is only practicable when the γ-sugars are ignored, we have not thought it necessary to discuss the limits of error of our empirical equations, and have therefore solved them as if the arbitrary constants which they contain were mathematically exact.

Empirical Equations for the Mutarotation Curves.

(*a*) *Numerical Data.*—The following data were available for the analysis of the mutarotation curves for aqueous solutions of α- and β-galactose at 20°.

TABLE I.

Mutarotation of α- and β-Galactose at 20°.

1. α-Galactose : first sample, recrystallised from 80% EtOH.

(*a*)	$2\frac{1}{2}$%	(4 dm.)	$\theta_0 = 16{\cdot}69$	$\theta_\infty = 9{\cdot}12$	$k_\infty = 0{\cdot}0187$
(*b*)	5%	(2 dm.)	$\theta_0 = 16{\cdot}55$	$\theta_\infty = 8{\cdot}92$	$k_\infty = 0{\cdot}0188$
(*c*)	10%	(2 dm.)	$\theta_0 = 31{\cdot}03$	$\theta_\infty = 17{\cdot}20$	$k_\infty = 0{\cdot}0189$
(*d*)	10%	(2 dm.)	$\theta_0 = 33{\cdot}09$	$\theta_\infty = 18{\cdot}15$	$k_\infty = 0{\cdot}0187$
(*e*)	15%	(2 dm.)	$\theta_0 = 45{\cdot}42$	$\theta_\infty = 24{\cdot}84$	$k_\infty = 0{\cdot}0186$
(*f*)	15%	(2 dm.)	$\theta_0 = 48{\cdot}88$	$\theta_\infty = 27{\cdot}20$	$k_\infty = 0{\cdot}0189$

2. α-Galactose : (*a*) second sample, recrystallised twice from 80% EtOH.
(*b*) third sample, recrystallised from acetic acid.
(*c*) fourth sample, recrystallised from acetic acid and 80% EtOH.

(*a*)	10%	(2 dm.)	$\theta_0 = 33{\cdot}63$	$\theta_\infty = 18{\cdot}80$	$k_\infty = 0{\cdot}0188$
(*b*)	10%	(2 dm.)	$\theta_0 = 34{\cdot}50$	$\theta_\infty = 18{\cdot}81$	$k_\infty = 0{\cdot}0189$
(*c*)	10%	(2 dm.)	$\theta_0 = 34{\cdot}71$	$\theta_\infty = 18{\cdot}91$	$k_\infty = 0{\cdot}0185$

3. β-Galactose : (a) precipitated by alcohol twice, and washed by 80% EtOH once.
(b) precipitated by alcohol twice, and washed by 80% EtOH twice.
(c) precipitated by alcohol twice, and washed by 80% EtOH six times.

(a) 5%	(2 dm.)	$\theta_0 = 6{\cdot}38$	$\theta_\infty = 9{\cdot}28$	$k_\infty =$	0·0191
(b) 5%	(2 dm.)	$\theta_0 = 6{\cdot}35$	$\theta_\infty = 9{\cdot}34$	$k_\infty =$	0·0183
(c) 7·7%	(2 dm.)	$\theta_0 = 9{\cdot}17$	$\theta_\infty = 14{\cdot}57$	$k_\infty =$	0·0192
					0·0188

In this table θ_0 is deduced by extrapolating the rotation of the solution to zero time, and θ_∞ by direct observation of the final rotatory power, whilst k_∞ is the velocity coefficient calculated from the later part of the mutarotation.

(b) *Preliminary Survey*.—Before making use of the general equations of Lowry and John it is desirable to make a preliminary enquiry as to the cause of the deviations from the unimolecular equations, which are found to satisfy, at least approximately, the data for glucose, but not for galactose.

(i) Two consecutive reversible unimolecular actions can give rise to unimolecular mutarotation curves only when $k_1 = k_3$, $k_2 = k_4$, and $\alpha + \beta = 2\mu$. Under these conditions, the general equations of Lowry and John reduce to the very simple form :

$$\theta_a = \tfrac{1}{2}(\alpha - \beta)e^{-k_1t} + \tfrac{1}{2}(\alpha + \beta)$$
$$\theta_\beta = -\tfrac{1}{2}(\alpha - \beta)e^{-k_1t} + \tfrac{1}{2}(\alpha + \beta)$$

The mutarotation then takes the form of a unimolecular change with velocity coefficient k_1, and covering a range of rotations from α or β to a final value $\tfrac{1}{2}(\alpha + \beta)$. Since k_2 does not enter into these equations at all, this statement is true for all concentrations of the intermediate sugar, which gives no indication whatever of its presence, in spite of the fact that it forms $100k_1/(k_1 + k_2)\%$ of the final equilibrium mixture, where this ratio may have any value from 0 to 100%.

(ii) If the rotatory power of the intermediate sugar is not the mean of the rotations of the α- and β-forms (although $k_1 = k_3$ and $k_2 = k_4$, as before), the equations become

$$\theta_a = \frac{\alpha - \beta}{2}e^{-k_1t} + \left\{\frac{\alpha + \beta}{2} - \mu\right\}\frac{k_1}{k_1 + 2k_2}e^{-(k_1+2k_2)t} + \frac{1}{k_1 + 2k_2}\left\{(\alpha + \beta)k_2 + \mu k_1\right\}$$

$$\theta_\beta = -\frac{\alpha - \beta}{2}e^{-k_1t} + \left\{\frac{\alpha + \beta}{2} - \mu\right\}\frac{k_1}{k_1 + 2k_2}e^{-(k_1+2k_2)t} + \frac{1}{k_1 + 2k_2}\left\{(\alpha + \beta)k_2 + \mu k_1\right\}$$

The second exponential term (which vanishes only when $\alpha + \beta = 2\mu$) *now persists; but since the coefficients of the two exponentials are* the same in both equations, although different in sign, these two *terms can be eliminated, one at a time, by adding or subtracting* the two equations, thus:

$$\theta_\alpha - \theta_\beta = (\alpha - \beta)e^{-k_1 t}$$

$$\theta_\alpha + \theta_\beta - 2\theta_\infty = (\alpha + \beta - 2\mu)\frac{k_1}{k_1 + 2k_2}e^{-(k_1 + 2k_2)t}$$

since $\theta_\infty = [(\alpha + \beta)k_2 + \mu k_1]/(k_1 + 2k_2)$.

If, therefore, the anomalous behaviour of galactose (as contrasted with glucose) were due exclusively to a deviation of the rotatory power of the intermediate sugar from the mean value for the α- and β-sugars, we could deduce a unimolecular coefficient for the *difference* of the rotatory powers of the α- and β-sugars, and so determine k_1, and then deduce a second unimolecular coefficient for the *average* of the rotatory powers, and so calculate the value of k_2 from the exponent $(k_1 + 2k_2)$. In this way we could obtain a complete solution of the problem, without making use of the general equations at all, and this simple test should obviously be applied in every case before the more complex procedure described below is adopted.

TABLE II.

Mutarotation of α- and β-Galactose.

(a) Difference. $\theta = \theta_\alpha - \theta_\beta$; $k = 0{\cdot}0188$; $\log\theta = -0{\cdot}008163t + 1{\cdot}3337$ (correct at 10 min.).				(b) Average. $\theta = \frac{1}{2}(\theta_\alpha + \theta_\beta) - \theta_\infty$; $k = 0{\cdot}0255$; $\log\theta = -0{\cdot}1108t + 0{\cdot}6386$ (correct at 5 min.).			
t.	θ (obs.).	θ (calc.).	Diff.	*t*.	θ (obs.).	θ (calc.).	Diff.
2	20·90	20·76	+0·14	2	4·35	4·13	+0·22
5	19·71	19·61	+0·10	5	3·83	3·83	0·00
10	17·87	17·87	0·00	10	3·23	3·37	−0·14
15	16·21	16·27	−0·06	15	2·82	2·96	−0·14
20	14·69	14·80	−0·11	20	2·58	2·61	−0·03
30	12·18	12·27	−0·09	30	2·09	2·02	+0·07
40	10·09	10·17	−0·08	40	1·72	1·57	+0·12
50	8·34	8·43	−0·09	50	1·42	1·22	+0·20
60	6·95	6·98	−0·03	60	1·15	0·94	+0·21
70	5·81	5·78	+0·03	70	0·91	0·73	+0·18
80	4·79	4·79	+0·00	80	0·75	0·57	+0·18
90	4·00	3·97	+0·03	90	0·62	0·44	+0·18
100	3·30	3·29	+0·01	100	0·52	0·34	+0·18

When this test is applied to α- and β-galactose, as in Table II, it can be seen at once that, whilst the *differences* conform very nearly the unimolecular law, the *averages* exhibit obvious systematic *ations, which are, however, also present in a less conspicuous* in the curve of differences. Whilst, therefore, the anomalous *ur of galactose may be attributed in the first instance to the*

fact that the rotatory power of the intermediate sugar approximates to that of the β-sugar, instead of to the average of the α- and β-sugars, it is clear that the velocity coefficients are also unsymmetrical, but to an extent which can only be disclosed by a complete mathematical analysis, since the small deviations recorded in Table II give no indication of the actual magnitude of this anomaly.

(*c*) *General Equations.*—Since none of the simplifying assumptions is possible in the case of galactose, it is necessary to fall back on the general equations for two consecutive unimolecular reactions. The empirical equations for the mutarotation of the α- and β-sugars then have the general form

$$\theta_\alpha = A_1 e^{-m_1 t} + B_1 e^{-m_2 t} + C; \quad \theta_\beta = A_2 e^{-m_1 t} + B_2 e^{-m_2 t} + C.$$

The number of exponential terms in these equations is equal to the number of consecutive changes which the sugars undergo; the identity of the exponents, and of the final constant C, expresses the fact that the sugars are undergoing the same series of changes (although in opposite directions) and give rise to the same final equilibrium mixture. It will be seen that these two equations, like the scheme on p. 669, include 7 arbitrary constants; if, therefore, equations of this type can be deduced for the mutarotation curves of the α- and β-sugars, it is theoretically possible to calculate from them the 7 fundamental constants of the original system, *viz.*, the four velocity coefficients k_1, k_2, k_3, k_4, and the rotatory powers α, μ, β, of the three sugars.

(*d*) *Initial Rotatory Power of α- and β-Galactose.*—The initial rotations of the α- and β-sugars are difficult to fix, since they depend, not only on the purity and dryness of the sugar, but on its homogeneity, *i.e.*, on the percentage of the α- and β-sugars which it contains; and even when the homogeneity of the material has been established, the initial rotations can only be deduced by extrapolation to a "zero-time," which is not very well defined, since there is always a little uncertainty as to the moment at which on the average the sugar entered into solution. We have therefore selected for α-galactose the value $[\alpha]_{5461} = 172{\cdot}5°$, and for β-galactose the value $[\alpha]_{5461} = 63{\cdot}5°$, as representing most closely the rotatory power of the sugars used in our experiments (compare Expts. 2*b* and 3*b* in Table I), although a slightly higher value for the initial and final rotations of α-galactose was given in Expt. 2*c*, where the concentration of the solution was perhaps a little greater. Since, however, the data for calculation were based on values for a 10% solution of the α-sugar in a 2 dm. tube or for a 5% solution of the β-sugar in a 4 dm. tube, the rotations in the empirical equation are one-fifth of the specific rotations. The initial rotations of the α-

and β-sugars, which do not enter directly into the equations, therefore lead to the relations

$\alpha = A_1 + B_1 + C = 34{\cdot}5°$ or $A_1 + B_1 = 15{\cdot}7°$ (since $C = 18{\cdot}8°$, see below);

$\beta = A_2 + B_2 + C = 12{\cdot}7°$ or $A_2 + B_2 = -6{\cdot}1°$.

(*e*) *Rotatory Power of the Equilibrium Mixture.*—The final specific rotations of the 12 solutions set out in Table I are as follows :

1. $[\alpha]_{5461} = 91°, 89°, 86°, 91°, 83°, 91°$.
2. $[\alpha]_{5461} = 94°, 94°, 95°$ } Mean 94°.
3. $[\alpha]_{5461} = 93°, 93°, 95°$ }

The first six values are irregular and low, perhaps on account of the presence of a variable proportion of alcohol in the first sample of the recrystallised sugar; but three further samples of α-galactose, and three samples of β-galactose give a uniform value $[\alpha]_{5461} = 94°$. The constant term in the two equations, which represents the final rotation of the solutions, has therefore the value $C = 18{\cdot}8°$.

(*f*) *Final Velocity Coefficients of α- and β-Galactose.*—Apart from the initial and final rotations, the easiest quantity to determine in these equations is the limiting value of the unimolecular velocity coefficient. Trustworthy values are obtained by ignoring the first half of the mutarotation of the α-sugar (where the coefficients are abnormally high), and the first third of the mutarotation of the β-sugar (where they are abnormally low), and treating the observations as if they had been begun 30 or 40 minutes after making up the solution (see col. 6 in Tables VI and VII). Since, as is shown below, the influence of the second term dies out after about ½ hour, this is a logical method for determining the value of the smaller exponent. It will also be recalled that Riiber and Minsaas obtained a constant unimolecular velocity coefficient (and therefore failed to discover the anomalous character of the mutarotation curves) as a result of adopting a similar procedure. In the present instance, the limiting value of the velocity coefficient, as deduced from the 12 experiments set out in Table I, is $m_1 = 0{\cdot}0188$, and this value can be inserted immediately in the equations as the exponent of the first term. When the true initial rotation of the α-sugar was used in calculating the unimolecular velocity coefficients, however, a slightly higher (but less trustworthy) limiting value was found, namely $k = 0{\cdot}0192$ (see col. 5 in Tables VI and VII), which agrees exactly with the mean of six values deduced from a study of three different properties of the two sugars by Riiber and Minsaas, *viz.*,

	k.	k_s.
Mutarotation of α-galactose	0·00834	0·0190
,, ,, β- ,, ...	0·00837	0·0193
Volume changes of α-galactose	0·00836	0·0192
,, ,, β- ,, ...	0·00845	0·0195
Refractivity of α-galactose	0·00822	0·0189
,, ,, β- ,, ...	0·00843	0·0194
		k_s at 20° = 0·0192

(*g*) *Initial Velocity Coefficient of* β-*Galactose*.—Since the rotatory power of β-galactose remains constant for about 4 minutes, $d\theta/dt = 0$, when $t = 0$; and since at this stage the only transformation is from the β-sugar to the intermediate (aldehydic) form, it follows that the rotatory power of these two sugars must be nearly the same, so that $\beta = \mu$ (approximately). This condition is, however, not sufficiently well-defined to be utilised in order to fix at once the value of the unknown rotatory power, μ, of the intermediate sugar (which is one of the objects of this research) and can only be used as evidence of the *approximate* equality of the rotatory power of the two sugars.

(*h*) *Initial Velocity Coefficient of* α-*Galactose*.—Although the initial stage of the mutarotation is obviously unimolecular rather than multimolecular, the velocity coefficients calculated by the ordinary method change so rapidly that it is not practicable to deduce a trustworthy initial value by extrapolating to zero time. Such a value can, however, be obtained by calculating from the rotations themselves an intermediate "end-point," to which the first stage of the mutarotation would lead if the second stage could be suspended. For this purpose we have used a formula given by Smith (*Phil. Mag.*, 1926, **1**, 496), *viz.*,

$$\alpha_\infty = \alpha_1 - (\alpha_1 - \alpha_2)^2/(2\alpha_2 - \alpha_1 - \alpha_3),$$

where α_1, α_2, α_3 are readings at equal increments of time, and α_∞ is the hypothetical end-point.

Four successive groups of three rotations at intervals of 2 minutes, read from a curve on which the readings for the first 10 minutes of Expt. 1*d* had been plotted, were found by this method to give

α_∞ = 22·5, 28·0, 26·7, 25·4; mean 25·6°. $[\alpha]_{5461}$ = 132·5°.*

A more accurate series of 5 sets of 3 readings, covering a total period of 7 minutes only, in Expt. 2*b* gave

α_∞ = 28·1, 27·6, 26·9, 26·3, 24·5; mean 26·7°. $[\alpha]_{5461}$ = 133·5°.

A third series of 4 sets of three readings (Expt. 2*c*), covering a period of 7½ minutes, gave

α_∞ = 26·9, 26·4, 27·8, 27·9; mean 27·25. $[\alpha]_{5461}$ = 136·2°.

* This value has been calculated by deducing the strength of the solution from its final rotatory power on the assumption that $[\theta_\infty]$ = 94°.

The last two series give a very uniform value for the end-point, $\alpha_\infty = 27°$, from which we can deduce that the specific rotatory power of the solution on completion of the first stage of the transformation would be $[\alpha]_{5461} = 135°$, as contrasted with the final equilibrium value $[\alpha]_{5461} = 94°$ at tbe end of the second stage.

This rotatory power is of the same order of magnitude as that assigned by Riiber and Minsaas to the intermediate sugar, *viz.*, $[\alpha]_D = 135°$, whence $[\alpha]_{5461} =$ about 153°; but it cannot be interpreted in this way, since, as we have seen, the intermediate form has nearly the same rotatory power as the β-sugar, whereas this is nearly equal to that of the α-sugar. A more plausible view, which we have not yet confirmed by mathematical analysis, is that the intermediate end-point, $[\alpha]_{5461} = 135°$, represents the rotatory power, not of the μ-sugar, but of an equilibrium mixture, $\alpha \rightleftharpoons \mu$, from which only the β-sugar is excluded.

By making use of this intermediate end-point, we obtain the velocity coefficients sbown in Table III. Tbe second of these series is not so consistent as the first, where the velocity coefficient is exceptionally uniform; but in both cases the data show clearly that the early stages of the mutarotation of α-galactose can be expressed quite satisfactorily as a unimolecular change, with velocity coefficient 0·064, and tending towards an end-point at $[\alpha]_{5461} = 135°$.

TABLE III.

Velocity Coefficients in the Early Stages of Mutarotation of α-Galactose.

t (min.).	$k_c \times 10^4$.	t (min.).	$k_c \times 10^4$.
2·15 + 0·95	640	2·65 + 0·95	624
+ 1·45	640	+ 1·30	602
+ 1·83	637	+ 1·93	611
+ 2·20	649	+ 2·37	624
+ 2·70	650	+ 2·78	643
+ 3·25	632	+ 3·23	645
+ 3·83	643	+ 3·68	639
+ 4·42	654	+ 4·17	650
+ 5·08	644	+ 4·67	650
+ 5·95	649	+ 5·17	648
+ 6·67	649	+ 5·68	651
+ 7·35	645	+ 6·25	658
Mean k_c = 0·0644		Mean k_c = 0·0637	

(*i*) *Calculations of Exponents and Coefficients.*—In order to determine the values of the coefficients A_1, B_1, A_2, B_2 of the empirical equations, and the unknown exponent m_2, we may notice that the velocity coefficients in the initial stages of the mutarotation of α- and β-galactose are given by

$$-d\theta/dt = A_1 m_1 + B_1 m_2 \text{ and } -d\theta/dt = A_2 m_1 + B_2 m_2.$$

If expressed as the velocity coefficient of a unimolecular action, with C as the limiting value, these quantities become

$$\frac{A_1m_1 + B_1m_2}{A_1 + B_1} \text{ and } \frac{A_2m_1 + B_2m_2}{A_2 + B_2}$$

Since the initial stages of the mutarotation of the α-sugar can be expressed as a unimolecular action with a velocity coefficient 0·064, and a range of 172°—135° = 37° (instead of 172° − 94° = 78°, when referred to the equilibrium value), the first of these expressions has the value 0·064 × 37 ÷ 78 = 0·030, whilst the second is approximately zero (see p. 675). Thus for the α-sugar we have

$$A_1 + B_1 = 15{\cdot}70 \text{ and } A_1m_1 + B_1m_2 = 15{\cdot}70 \times 0{\cdot}030 = 0{\cdot}48,$$

whilst for the β-sugar

$$A_2 + B_2 = -6{\cdot}1 \text{ and } A_2m_1 + B_2m_2 = 0 \text{ (approximately)},$$

where in each equation $m_1 = 0{\cdot}0188$. If therefore m_2 were known, we could now calculate the four remaining coefficients, A_1, B_1, A_2, B_2, of the empirical equations from these four relationships. Alternatively, we can eliminate m_2, B_1, and B_2 from these relations and so obtain

$$0{\cdot}115A_1 - 0{\cdot}181A_2 - 2{\cdot}91 = 0 \quad . \quad . \quad . \quad (1)$$

Since only the ends of the mutarotation curves have been used hitherto, the additional datum that is required to complete the analysis can be brought in most easily by reading off the values of θ for each sugar at a time (*e.g.*, 20 minutes) when mutarotation is less than half-complete. Thus since $\theta_\alpha = 28{\cdot}68$ and $\theta_\beta = 13{\cdot}99$ when $t = 20$ (and consequently $e^{-m_1t} = 0{\cdot}6865$) we can write:

$$0{\cdot}6865A_1 + B_1e^{-m_2t} + C = 28{\cdot}68$$
$$0{\cdot}6865A_2 + B_2e^{-m_2t} + C = 13{\cdot}99$$

or, since $B_1 = 15{\cdot}70 - A_1$, $B_2 = -6{\cdot}10 - A_2$, $C = 18{\cdot}80$, we can eliminate m_2 and obtain

$$-0{\cdot}622A_1 + 0{\cdot}898A_2 + 15{\cdot}2 = 0 \quad . \quad . \quad . \quad (2)$$

Similar equations can be deduced from the values of θ_α and θ_β at any other values of t, but, when t is large, the ratios involved approximate to zero and therefore become of very little value.

Equations (1) and (2) can now be combined to give A_1 and A_2, and hence B_1, B_2, and m_2. Unfortunately, these eliminations result in an exaggeration of the experimental errors which make it almost a matter of accident whether they yield a plausible solution of the problem or not. The combination of data which we happened to use gave values for the coefficients which required very little adjustment to make them fit the curves, the adjusted values being

$m_2 = 0{\cdot}146$, $A_1 = 14{\cdot}3$, $B_1 = 1{\cdot}4$, $A_2 = -7{\cdot}13$, $B_2 = 1{\cdot}03$; but as a different selection of data gave $B_2 = 0$ (in which case the mutarotation curve of the α-sugar would have been unimolecular), we think it desirable to describe an alternative procedure, which does not depend on the selection of a single pair of readings but is based upon a general average of a series.

Table IV.

Determination of Coefficients.

t.	θ_α.	A_1.		θ_β.	A_2.	
2	33·60	15·48		12·70	−6·33	
5	32·49	15·04		12·78	−6·61	
10	30·97	14·69		13·10	−6·88	
15	29·73	14·49		13·52	−7·00	
20	28·68	14·40		13·99	−7·01	
30	26·95	14·33		14·80	−7·03	
40	25·57	14·36		15·48	−7·04	−7·1
50	24·39	14·31	14·31	16·05	−7·04	
60	23·43	14·30		16·48	−7·16	
70	22·62	14·25		16·86	−7·23	
80	—	—		17·16	−7·29	

Table V.

Mutarotation of α- and β-Galactose.

t.	θ_α (obs.).	θ_α (calc.).	Diff.
0	34·50*	14·30 + 1·40 + 18·80 = 34·50	0·00
2	33·60	13·77 + 1·05 + 18·80 = 33·62	−0·02
5	33·49	13·02 + 0·67 + 18·80 = 32·49	0·00
10	30·97	11·84 + 0·32 + 18·80 = 30·96	+0·01
15	29·73	10·78 + 0·16 + 18·80 = 29·74	−0·01
20	28·68	9·81 + 0·07 + 18·80 = 28·68	0·00
30	26·98	8·13 + 0·02 + 18·80 = 26·95	+0·03
40	25·57	6·74 + — + 18·80 = 25·54	+0·03
50	24·39	5·59 + — + 18·80 = 24·39	0·00
60	23·43	4·63 + — + 18·80 = 23·43	0·00
70	22·62	3·83 + — + 18·80 = 22·63	−0·01
80	21·95	3·18 + — + 18·80 = 21·98	−0·03
100	20·97	2·18 + — + 18·80 = 20·98	−0·01
t.	θ_β (obs.).	θ_β (calc.).	Diff.
0	12·70*	−7·13 + 1·03 + 18·80 = 12·70	0·00
2	12·70	−6·87 + 0·77 + 18·80 = 12·70	0·00
5	12·78	−6·46 + 0·50 + 18·80 = 12·84	−0·06
10	13·10	−5·91 + 0·24 + 18·80 = 13·13	−0·03
15	13·52	−5·38 + 0·12 + 18·80 = 13·54	−0·02
20	13·99	−4·89 + 0·06 + 18·80 = 13·97	+0·02
30	14·80	−4·06 + 0·01 + 18·80 = 14·75	+0·05
40	15·48	−3·33 + — + 18·80 = 15·48	0·00
50	16·05	−2·79 + — + 18·80 = 16·02	+0·03
60	16·48	−2·31 + — + 18·80 = 16·51	−0·03
70	16·86	−1·91 + — + 18·80 = 16·89	−0·03
80	17·16	−1·59 + — + 18·80 = 17·21	−0·05
[illegible]	17·67	−1·01 + — + 18·80 = 17·69	−0·02

* By extrapolation.

This procedure depends upon the fact that one exponential dies out before the other, after which the mutarotation becomes unimolecular and gives rise to steady velocity coefficients. We can therefore extrapolate back to a hypothetical initial value at zero time, on the assumption that the second exponential is not present, and so obtain values of A_1 or A_2 from the expressions

$$A_1 = (\theta_a - \theta_\infty)/e^{-0\cdot0188t}; \quad A_2 = (\theta_\beta - \theta_\infty)/e^{-0\cdot0188t}.$$

TABLE VI.

Mutarotation of α-Galactose in Water at 20°.

(*a*) Second sample (recryst. HAc), 10 g./100 c.c. in 2 dm. tube.

$$\theta_a = 13\cdot62e^{-0\cdot0188t} + 1\cdot21e^{-0\cdot146t} + 18\cdot80.$$

	θ_{5461}.				
t (min.).	obs.	calc.	Diff.	k.	k_1.
2·15	32·80	32·78	+0·02		
2·70	32·58	32·56	+0·02	0·0285	
3·10	32·44	32·41	+0·03	0·0274	
3·60	32·26	32·24	+0·02	0·0272	
3·98	32·13	32·12	+0·01	0·0267	
4·35	31·99	31·99	0·00	0·0271	
4·85	31·82	31·83	−0·01	0·0269	
5·40	31·67	31·65	+0·02	0·0259	
5·98	31·47	31·48	−0·01	0·0260	
6·57	31·27	31·29	−0·02	0·0262	
7·23	31·10	31·10	0·00	0·0255	
8·10	30·85	30·87	−0·02	0·0252	
8·82	30·66	30·67	−0·01	0·0248	
9·50	30·50	30·49	+0·01	0·0244	
10·70	30·16	30·19	−0·03	0·0244	
12·30	29·78	29·81	−0·03	0·0239	
13·22	29·59	29·60	−0·01	0·0235	
15·15	29·16	29·17	−0·01	0·0232	
17·00	28·77	28·80	−0·03	0·0229	
19·83	28·24	28·25	−0·01	0·0223	
22·15	27·81	27·83	−0·02	0·0220	
24·28	27·46	27·47	−0·01	0·0217	
26·97	27·02	27·02	0·00	0·0215	
30·17	26·55	26·53	+0·02	0·0211	
33·23	26·10	26·08	+0·02	0·0210	
36·55	25·65	25·65	0·00	0·0208	0·0191
40·15	25·21	25·20	+0·01	0·0206	0·0188
43·28	24·85	24·84	+0·01	0·0204	0·0187
47·35	24·40	24·39	+0·01	0·0203	0·0188
54·67	23·67	23·67	0·00	0·0201	0·0189
63·00	22·96	22·97	−0·01	0·0196	0·0183
70·17	22·45	22·40	+0·05	0·0198	0·0188
82·28	21·71	21·70	+0·01	0·0196	0·0188
92·15	21·21	21·21	0·00	0·0196	0·0187
105·95	20·65	20·64	+0·01	0·0195	0·0189
122·73	20·14	20·15	−0·01	0·0195	0·0189
150·00	19·63	19·61	+0·02	0·0191	0·0186
∞	18·80	18·80	0·00		

(*b*) Third sample (recryst. HAc and EtOH), 10 g./100 c.c. in 2 dm. tube.

$$\theta_a = 14{\cdot}33e^{-0{\cdot}0188t} + 1{\cdot}40e^{-0{\cdot}146t} + 18{\cdot}81.$$

	θ_{5461}				
t (min.).	obs.	calc.	Diff.	*k*.	k_e.
2·65	33·36	33·40	−0·04		
3·60	33·01	33·03	−0·02	0·0257	
3·95	32·90	32·89	+0·01	0·0250	
4·58	32·68	32·68	0·00	0·0247	
5·02	32·52	32·52	0·00	0·0252	
5·43	32·36	32·38	−0·02	0·0257	
5·88	32·21	32·23	−0·02	0·0255	
6·33	32·08	32·09	−0·01	0·0250	
6·82	31·91	31·94	−0·03	0·0252	
7·32	31·76	31·78	−0·02	0·0250	
7·82	31·62	31·63	−0·01	0·0247	
8·33	31·47	31·47	0·00	0·0245	
8·90	31·30	31·31	−0·01	0·0245	
9·48	31·14	31·15	−0·01	0·0243	
10·20	30·95	30·96	−0·01	0·0240	
11·47	30·62	30·62	0·00	0·0237	
12·38	30·38	30·39	−0·01	0·0236	
13·53	30·11	30·11	0·00	0·0232	
15·37	29·70	29·68	+0·02	0·0228	
17·75	29·19	29·18	+0·01	0·0224	
20·33	28·67	28·66	+0·01	0·0220	
22·62	28·23	28·23	0·00	0·0218	
26·03	27·64	27·62	+0·02	0·0214	
30·35	26·94	26·92	+0·02	0·0210	
36·05	26·12	26·09	+0·03	0·0206	
44·47	25·06	25·02	+0·04	0·0202	0·0186
53·87	24·05	24·01	+0·04	0·0199	0·0187
61·85	23·29	23·29	0·00	0·0199	0·0190
77·83	22·11	22·13	−0·02	0·0197	0·0190
89·25	21·49	21·49	0·00	0·0195	0·0189
101·75	20·91	20·93	−0·02	0·0195	0·0190
112·52	*20·51*	*20·54*	*−0·03*	*0·0195*	*0·0191*
∞	18·81	18·81	0·00		

The data set out in Table IV give for A_1 the trustworthy value 14·3; B_1 must then have the value 1·4, since $A_1 + B_1 = 15{\cdot}7$. Moreover, since $14{\cdot}3 \times 0{\cdot}0188 + 1{\cdot}4m_2 = 0{\cdot}48$, it follows at once that $m_2 = 0{\cdot}148$, in close agreement with the value 0·146 which we had already found to fit the curves. The extrapolated values for A_2 vary very little after the first 10 minutes; a long series of values is then obtained with an average $A_2 = -7{\cdot}1$, which agrees closely with the coefficient −7·13 which we had found to fit the curves. Since $A_2 + B_2 = -6{\cdot}1$, the value of B_2 must be 1·0 approximately, but a slight adjustment is needed to get the inflexion into the right position, and this adjustment leads to a small negative value (instead of an exact zero value) for $d\theta/dt$ for the β-sugar when $t = 0$.

(*j*) *Empirical Equations for the Mutarotation of* α- *and* β-*Galactose.* —The empirical equations as finally adjusted are

$$\theta_\alpha = 14{\cdot}30e^{-0{\cdot}0188t} + 1{\cdot}40e^{-0{\cdot}146t} + 18{\cdot}80$$
$$\theta_\beta = -7{\cdot}13e^{-0{\cdot}0188t} + 1{\cdot}03e^{-0{\cdot}146t} + 18{\cdot}80.$$

The extent of the agreement with the interpolated values for the rotatory powers of the two sugars at equal increments of time is shown in Table V. This table also shows how the influence of the second exponential disappears after about 30 minutes, when the curves assume a unimolecular form, as Riiber and Minsaas observed. The agreement between the original readings and values calculated from the equations is shown in Tables VI and VII.

TABLE VII.

Mutarotation of β-*Galactose in Water at* 20°.

(*a*) First sample (washed once), 5 g./100 c.c. in 2 dm. tube.

$$\theta_\beta = -3{\cdot}20e^{-0{\cdot}0188t} + 0{\cdot}30e^{-0{\cdot}146t} + 9{\cdot}28.$$

	θ_{5461}.				
t (min.).	obs.	calc.	Diff.	k.	k_r.
1·75	6·51	6·41	+0·10		
2·53	6·48	6·44	+0·04		
3·13	6·48	6·45	+0·03		
3·73	6·48	6·47	+0·01		
4·82	6·48	6·51	−0·03		
5·73	6·52	6·54	−0·02		
7·23	6·56	6·59	−0·03	0·0053	
8·08	6·58	6·62	−0·04	0·0057	
9·23	6·64	6·67	−0·03	0·0079	
10·47	6·67	6·71	−0·04	0·0081	
12·33	6·75	6·79	−0·04	0·0096	
13·87	6·82	6·85	−0·03	0·0099	
16·47	6·93	6·96	−0·03	0·0119	
18·28	6·99	7·03	−0·04	0·0122	
20·23	7·09	7·10	−0·01	0·0133	
22·25	7·18	7·18	0·00	0·0140	
24·35	7·27	7·26	+0·01	0·0147	
26·38	7·33	7·33	0·00	0·0147	
29·20	7·45	7·43	+0·02	0·0155	
32·35	7·55	7·54	+0·01	0·0157	0·0192
37·33	7·69	7·69	0·00	0·0159	0·0184
41·53	7·82	7·81	+0·01	0·0160	0·0188
45·28	7·93	7·91	+0·02	0·0168	0·0192
49·73	8·06	8·02	+0·04	0·0173	0·0198
54·85	8·16	8·14	+0·02	0·0173	0·0193
59·53	8·27	8·23	+0·04	0·0177	0·0196
69·13	8·42	8·41	+0·01	0·0175	0·0190
80·88	8·58	8·58	0·00	0·0175	0·0187
89·20	8·71	8·68	+0·03	0·0182	0·0190
117·42	8·95	8·93	+0·02	0·0185	0·0194
∞	9·28	9·28	0·00		

(*b*) Second sample (washed twice), 5 g./100 c.c. in 2 dm. tube.

$$\theta_\beta = -3{\cdot}56e^{-0{\cdot}0188t} + 0{\cdot}51e^{-0{\cdot}146t} + 9{\cdot}34.$$

	θ_{5461}.				
t (min.).	obs.	calc.	Diff.	k.	k_e.
1·92	6·31	6·29	+0·02		
2·48	6·31	6·30	+0·01		
2·88	6·32	6·30	+0·02		
3·32	6·31	6·30	+0·01		
3·90	6·31	6·32	−0·01		
4·42	6·32	6·33	−0·01		
4·95	6·35	6·34	+0·01		
5·83	6·35	6·36	−0·01		
6·53	6·36	6·38	−0·02		
7·60	6·40	6·42	−0·02	0·0053	
8·80	6·46	6·46	0·00	0·0074	
9·95	6·51	6·51	0·00	0·0085	
11·50	6·54	6·55	−0·01	0·0082	
12·37	6·59	6·59	0·00	0·0093	
14·10	6·68	6·68	0·00	0·0107	
16·00	6·76	6·75	+0·01	0·0114	
18·03	6·86	6·84	+0·02	0·0124	
20·33	6·95	6·94	+0·01	0·0129	
22·43	7·04	7·02	+0·02	0·0134	
24·53	7·13	7·10	+0·03	0·0140	
26·68	7·22	7·19	+0·03	0·0144	
28·58	7·28	7·26	+0·02	0·0145	
29·43	7·32	7·30	+0·02	0·0147	
32·12	7·43	7·44	−0·01	0·0153	
35·32	7·52	7·51	+0·01	0·0153	0·0184
39·15	7·64	7·63	+0·01	0·0152	0·0182
42·85	7·76	7·75	+0·01	0·0159	0·0185
47·00	7·88	7·87	+0·01	0·0162	0·0193
51·17	7·98	7·98	0·00	0·0163	0·0190
58·78	8·16	8·16	0·00	0·0166	0·0184
64·23	8·27	8·27	0·00	0·0167	0·0179
69·27	8·35	8·37	−0·02	0·0166	0·0173
77·92	8·50	8·51	−0·01	0·0169	0·0182
90·72	8·67	8·69	−0·02	0·0170	0·0181
109·17	8·85	8·86	−0·01	0·0170	0·0178
∞	9·34	9·34	0·00		

Evaluation of the Fundamental Constants.

The empirical equations set out above provide a complete summary of the experimental data, and it is impossible to deduce from these data anything that is not contained in the equations. Whilst, however, it is easy to work out the seven constants of the empirical equations when the seven fundamental constants of the system are known, it is not easy to carry out the converse process, on account of the complex form in which the fundamental constants appear in the equations. (i) The simplest relationships are found in the exponents, which depend only on the velocity coefficients of the sugars, and not on their optical rotations. These relationships can

e summarised most concisely by means of the two following quations :

$$k_1+k_2+k_3+k_4=m_1+m_2=0{\cdot}0188+0{\cdot}146=0{\cdot}1648 \quad . \quad . \quad (3)$$
$$k_2k_3+k_1k_3+k_1k_4=m_1m_2=0{\cdot}0188\times 0{\cdot}146=0{\cdot}002745 \quad . \quad . \quad (4)$$

(ii) The coefficients of the empirical equations* are more complex functions, since they depend on the rotations as well as the velocity coefficients of the sugars. They may, however, be summarised as follows :

$$C = \alpha x_\infty + \mu y_\infty + \beta z_\infty = 18{\cdot}80$$

$$A_1 = -\frac{m_2}{m_2-m_1}C + \frac{m_2}{m_2-m_1}\alpha - \frac{k_1}{m_2-m_1}(\alpha-\mu) = 14{\cdot}30$$

$$B_1 = \frac{m_1}{m_2-m_1}C - \frac{m_1}{m_2-m_1}\alpha + \frac{k_1}{m_2-m_1}(\alpha-\mu) = 1{\cdot}40$$

$$A_2 = -\frac{m_2}{m_2-m_1}C + \frac{m_2}{m_2-m_1}\beta - \frac{k_3}{m_2-m_1}(\beta-\mu) = -7{\cdot}13$$

$$B_2 = \frac{m_1}{m_2-m_1}C - \frac{m_1}{m_2-m_1}\beta + \frac{k_3}{m_2-m_1}(\beta-\mu) = 1{\cdot}03$$

f we add these equations in pairs we merely get the former relations $A_1 + B_1 + C = \alpha$; and $A_2 + B_2 + C = \beta$. If, however, we subract them we get

$$A_1 - B_1 = \frac{m_2+m_1}{m_2-m_1}(\alpha - C) - \frac{2k_1}{m_2-m_1}(\alpha-\mu) = 12{\cdot}9$$

$$A_2 - B_2 = \frac{m_2+m_1}{m_2-m_1}(\beta - C) - \frac{2k_3}{m_2-m_1}(\beta-\mu) = -8{\cdot}16$$

r

$$k_1(\alpha-\mu) = \tfrac{1}{2}(m_2+m_1)(\alpha-C) - \tfrac{1}{2}(m_2-m_1)\,12{\cdot}9 = 0{\cdot}4732 \qquad (5)$$
$$k_3(\beta-\mu) = \tfrac{1}{2}(m_2+m_1)(\beta-C) + \tfrac{1}{2}(m_2-m_1)\,8{\cdot}16 = 0{\cdot}01634 \qquad (6)$$

vhere numerical values for $k_1(\alpha-\mu)$ and $k_3(\beta-\mu)$ have been leduced by inserting $m_2+m_1=0{\cdot}1648$, $m_2-m_1=0{\cdot}1272$, $\alpha - C = 15{\cdot}7$, $\beta - C = -6{\cdot}1$.

(iii) The fifth relation that is required to give the four unknown velocity coefficients and the unknown rotation μ, is supplied by

$$\theta_\infty = \alpha x_\infty + \mu y_\infty + \beta z_\infty$$

r

$$C = \frac{\alpha k_2k_3 + \mu k_1k_3 + \beta k_1k_4}{k_2k_3+k_1k_3+k_1k_4}$$

vhence $$(\alpha - C)k_2k_3 + (\mu - C)k_1k_3 + (\beta - C)k_1k_4 = 0$$

* The coefficients for θ_β are got by substituting k_3 for k_1 and β for α, since he m's are reversible functions of the k's.

or, dividing by k_1k_3,

$$\mu = C - (\alpha - C)\frac{k_2}{k_1} - (\beta - C)\frac{k_4}{k_3} = 18{\cdot}8 - 15{\cdot}7\frac{k_2}{k_1} + 6{\cdot}1\frac{k_4}{k_3} \quad . \quad (7)$$

(iv) The simplest way of proceeding from this point is to assume a value of μ, and then to deduce k_1 and k_3 from (5) and (6). Substitution in (3) gives $k_2 + k_4$, which can be combined with (7) (after a similar substitution) to give k_2 and k_4. The sum of the products in (4) can then be evaluated and compared with the observed value $m_1m_2 = 0{\cdot}002745$. By this method of trial and error, we find that μ has the value 11·67, and that, if we alter it only to 11·65, an erroneous value (0·002726 instead of 0·002745) is obtained for m_1m_2. We can therefore assign to the intermediate sugar the specific rotation $[\alpha]_{5461} = 58°$ if we accept the validity of the three-sugar scheme. The corresponding values of the velocity coefficients are :

$$k_1 = 0{\cdot}0207 \qquad k_3 = 0{\cdot}0159$$
$$k_2 = 0{\cdot}0494 \qquad k_4 = 0{\cdot}0788$$
$$k_1 + k_2 = 0{\cdot}0701 \qquad k_3 + k_4 = 0{\cdot}0947$$

Equilibrium Concentrations and Rotations.

The equilibrium concentrations deduced from the velocity coefficients of the three-sugar scheme are

$$x_\infty = 28{\cdot}5\%;\ y_\infty = 12{\cdot}0\%;\ z_\infty = 59{\cdot}5\%.$$

These can be compared with the values deduced by Riiber and Minsaas, *viz.*,

$$x_\infty = 6{\cdot}61\%;\ y_\infty = 27{\cdot}35\%;\ z_\infty = 66{\cdot}04\%.$$

A similar comparison of the optical rotations of the three sugars gives

		α.	μ.	β.	
	$[\alpha]_{5461}=$	173°	58°	63·5°	(Lowry and Smith)
	$[\alpha]_D =$	144·5°	135·0°	52·2°	(Riiber and Minsaas)
or	$[\alpha]_{5461}=$	173·4°	162°	62·6°	

if we increase the values of $[\alpha]_D$ by 20%* to allow for the change of wave-length.

Since Riiber and Minsaas did not detect any anomalies in the mutarotation curves, their estimate of the rotatory power of the intermediate sugar is based on less direct evidence than our own, and is obviously incorrect in making this rotation approximate to that of α-galactose, whereas actually it does not differ much from

* This is greater than the observed increment, but has been selected because it gives the best agreement in the case of the α- and β-sugars.

that of β-galactose. Their equations also lead to an abnormally *slow* mutarotation of *α-galactose in the early stages (corresponding to the small change of rotation from α to μ)*, whereas in fact the mutarotation is exceptionally *fast* at this stage.

On the assumption that only 3 isomerides are present, our estimate of the percentages of the three sugars in the equilibrium mixture is probably correct to within a few units, since it is based on data in which the effects of the third sugar are very obvious. It has the advantage of raising the proportion of the α-sugar to a more reasonable figure than that given by Riiber and Minsaas, namely 28·5% instead of only 6·6%. The proportion of the intermediate open-chain sugar, on the other hand, is reduced from 27% to 12% of the total. The two estimates concur, however, in making the β-sugar the predominant constituent, forming 60 to 66% of the equilibrium mixture.

Since the equilibrium proportion of α-galactose in anhydrous methyl alcohol is about 1/2 of the total (J., 1904, **85**, 1557), the ratio β/α cannot be greater than unity in this solvent; it is therefore surprising to find a ratio $\beta/\alpha > 2/1$ in water. This wide difference may be due to a selective action of water in promoting the formation of β-galactose at the expense of the α-sugar; but, on the other hand, it may be merely a proof that the equilibrium in aqueous solutions is too complex to be represented by the simple system which must be postulated if a mathematical analysis of the data is to be carried out. Whilst, therefore, we have sought to make the fullest possible use of this mathematical analysis, and to follow up all the consequences which flow from its application to our data, our positive assertions do not go beyond the simple facts set out in the following summary, *viz.*, that: (i) The mutarotation data for galactose cannot be interpreted on a 2-sugar scheme, but can be expressed by a 3-sugar scheme; (ii) a third sugar must therefore be formed in substantial quantities in solution; (iii) this sugar must be related unsymmetrically to the α- and β-sugars, in rotation or in velocity of formation and reversion, or in both; (iv) since the mutarotation of β-galactose proceeds only very slowly during the first few minutes, and gives rise to inflected curves, the initial product of change must have a similar rotation to the β-sugar.

We are indebted to Messrs. Bromwich, White, and Constable, of St. John's College, for assistance in the mathematical analysis set out above, and desire to take this opportunity of expressing our thanks.

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XCII.—*The Competitive Interaction of Alkyl and Aryl Halides with Magnesium.*

By Herbert William Rudd and Eustace Ebenezer Turner.

Measurements of the reactivity of alkyl halides have hitherto been made using five different types of reagent : (1) Sodium meth-, eth-, or *n*-prop-oxide (Hecht, Conrad, and Brückner, *Z. physikal. Chem.*, 1889, **4**, 273), sodium phenoxide (Segaller, J., 1913, **103**, 1154), sodium α- and β-naphthoxides (Cox, J., 1918, **113**, 666) and sodium benzyloxide (Heywood, J., 1922, **121**, 1904). (2) Ethyl sodiomalonate or -acetoacetate (Wislicenus, *Annalen*, 1882, **212**, 239). (3) Various tertiary bases (Menschutkin, *Z. physikal. Chem.*, 1890, **5**, 589; Wedekind, *Annalen*, 1901, **318**, 90; Preston and Jones, J., 1912, **101**, 1930). (4) Alcoholic silver nitrate (Burke and Donnan, J., 1904, **85**, 555; *Z. physikal. Chem.*, 1909, **69**, 148). (5) Sodium thiosulphate (Slator, J., 1904, **85**, 1286).

Although these different reagents would not be expected to give a similar order of reactivity for a series of alkyl halides, a number of general conclusions may be drawn. Methyl iodide is far more reactive than ethyl iodide, and the latter much more reactive than *n*-propyl iodide (Menschutkin, Segaller, Cox, Heywood, and Hecht, Conrad, and Brückner). Burke and Donnan found that methyl and *n*-propyl iodides reacted at approximately the same rate, which was less than that for ethyl iodide, and not much greater than that for *n*-butyl iodide. The reaction between iodides and alcoholic silver nitrate is, however, complicated, as Burke and Donnan pointed out. Wislicenus found that ethyl and *n*-propyl iodides were respectively very much more reactive than the corresponding bromides, and that benzyl bromide was much more reactive than the chloride. Menschutkin found ethyl, *n*-propyl, *n*-butyl, *n*-heptyl and *n*-octyl iodides to be more reactive than the bromides. Slator concluded that bromides and iodides were almost equally reactive, and very much more reactive than the corresponding chlorides.

No measurements have hitherto been made of the reactivities of simple halogen derivatives of aromatic hydrocarbons. Indeed, there are very few reactions which could be used for such measurements. Certain facts were known, *e.g.*, that iodobenzenes react with copper bronze (Ullmann reaction), whereas bromo- and chloro-compounds do so much less readily; further, that whereas bromo- and iodo-benzene readily combine with magnesium, chlorobenzene does not. The formation of the Grignard reagent has now been found to afford a convenient method for comparing "reactivities" of both aliphatic and aromatic halogen compounds.

Our procedure has been to allow a mixture of two different halogen derivatives (1 mol. of each) to compete, under certain definite conditions, for one atom of magnesium, and to analyse the product when complete dissolution of the metal had occurred. Ordinary "Grignard" magnesium turnings were used. The slight difference in surface area and condition between one sample and another introduces no material error, since after the first few minutes of reaction the condition of the metallic surface in one experiment is little different from that in another, and moreover, both halides will presumably benefit or suffer to the same extent.

By using specially standardised magnesium, even more accurate results would possibly be attainable. Our purpose, however, has been, not to obtain absolute values of the reactivities, but to compare reactivities to a reasonably quantitative degree. The method is capable of general application, and is being extended.

In discussing our results, the fact must not be overlooked that two other reactions may accompany the formation of a Grignard reagent: (*a*) $RMgX + RX = MgX_2 + R{\cdot}R$ and (*b*) $2RX + Mg = MgX_2 + R{\cdot}R$. It seems probable that (*b*) is realised usually through (*a*). Di-alkyl and di-aryl hydrocarbons are formed to any large extent, however, only with particular types of halogen compound when conditions such as have been used for the present work obtain.

A trace of iodine was sometimes necessary to start the reaction. This vitiates the results to the extent only of 0·02% (see Experimental).

It is possible that the reactivity of one halide may be affected by the presence of another more reactive halide. We found as a limiting case that magnesium did not react with chlorobenzene even when a vigorous combination of the metal with bromobenzene was in progress.

The results obtained are in Tables I and II. The figures given under "%Br," "%Cl," etc., refer to the percentage of bromine and chlorine respectively which, at the completion of a reaction, had combined with the magnesium.

These figures show many interesting features. In the first place, when bromide–chloride pairs compete for magnesium, the bromide, at first the more reactive, becomes relatively more reactive as one passes from ethyl to butyl. A mixture of methyl chloride and bromide could not be made to react with magnesium. On the other hand, with iodide–chloride pairs, the initially more reactive iodide decreases in reactivity with ascent from methyl to butyl, and with bromide–iodide pairs an alternation is observed.

TABLE I.

	% Br.	% Cl.		% I.	% Cl.		% Br.	% I.
MeBr–MeCl	—	—	MeI–MeCl	73	27	MeBr–MeI	71	29
EtBr–EtCl	76	24	EtI–EtCl	71	29	EtBr–EtI	46	54
$Pr^{α}$Br–$Pr^{α}$Cl	81	19	$Pr^{α}$I–$Pr^{α}$Cl	56	44	$Pr^{α}$Br–$Pr^{α}$I	57	43
$Bu^{α}$Br–$Bu^{α}$Cl	91	9	$Bu^{α}$I–$Bu^{α}$Cl	54	46	$Bu^{α}$Br–$Bu^{α}$I	27	73

	% Br.	% I.		% Br.	% Cl.
PhBr–PhI	52	48	$Bu^{α}$Br–CH_2PhCl	73	27
o-C_6H_4MeBr–*o*-C_6H_4MeI	94	6			
m-C_6H_4MeBr–*m*-C_6H_4MeI	88	12			
p-C_6H_4MeBr–*p*-C_6H_4MeI	84	16			

TABLE II.

Analysis of results for aliphatic compounds. Relative reactivities.

Alkyl radical present.	Br.	I.	Br.	Cl.	I.	Cl.
Me	2·5	1	—	—	2·7	1
Et	0·8	1	3·2	1	2·5	1
$Pr^{α}$	1·3	1	4·3	1	1·3	1
$Bu^{α}$	0·4	1	9·9	1	1·2	1

Consideration of the results obtained with the four aromatic pairs suggests that the introduction of a methyl group into the nucleus of bromobenzene increases the reactivity of the halogen atom, and that the reverse effect occurs with iodobenzene. We hope to elaborate this point later and correlate the results with such facts as the greater speed of nitration of toluene as compared with benzene, etc. (compare Wibaut, *Rec. trav. chim.*, 1915, **34**, 241).

The effect of a methyl group on the reactivity of a halogen atom appears to be little dependent on the relative positions of the two atoms, although the bromine/iodine reactivity ratio decreases in the order $o > m > p$.

In view of the greatly increased activity associated with the introduction of a methyl group into bromobenzene, the three chlorotoluenes might be expected to react with magnesium. We find that they do react to some extent with magnesium which has previously been treated with iodine or with ethereal methyl iodide, but that the reaction soon becomes very slow. Moreover, from the fact that the resulting solution does not decolorise ethereal iodine solution, it may be inferred that what reaction does occur is of type (*b*) above (ditolyl formation). *cyclo*Hexyl halides were also found to react to a considerable extent in the sense of equation (*b*), although Grignard reagent formation occurs to a large extent in addition.

One of the most interesting results obtained is that bromine compounds appear on the whole to combine more readily with magnesium than do the corresponding iodine compounds.

EXPERIMENTAL.

Preparation and Purification of Reagents.—The liquid alkyl halides were purified by routine processes and distilled at least twice just before use, the first and last runnings being rejected. The aromatic halogen compounds were prepared for the purpose and purified by routine processes.

Method.—In most cases, the quantities used were 1/40 molar. Equimolecular amounts of each halide were taken, magnesium in the same proportion, *i.e.*, 1 : 1 : 1, and a fixed amount of ether (50 c.c. in a 1/40 molar experiment). The magnesium was placed in a litre round-bottom flask, fitted with a reflux condenser and dropping-funnel, suitable precautions being taken against the ingress of water and carbon dioxide. The halides were washed into the funnel with a little ether and run into the flask, and the rest of the ether was added in the same way. Iodine (not more than 1·5 mg., corresponding to 1/200,000 mol. of Grignard reagent) was added after a short time if the reaction did not start spontaneously. The flask was kept well shaken until no further reaction occurred, and the solution was at no time allowed to boil vigorously. The reactions were complete in 2—4 hours. The mixture was then treated with water, and with very dilute sulphuric acid. The ethereal layer was separated and washed with water, and the aqueous part together with the washings boiled to expel dissolved ether. This solution was then analysed.

For very volatile halides, the reaction was carried out in a stout glass bottle of about 400 c.c. capacity, fitted with a ground glass stopper, the halides being introduced, and the stopper then tightly closed. It was not removed until the mixture was decomposed with water.

The gaseous halides were stored over brine. The required volume of gas, 560 c.c. at *N.T.P.* corresponding to 1/40 mol., corrected to prevailing conditions, was measured in a gas pipette, and displaced through two phosphoric oxide drying tubes into a spiral condenser surrounded with ice and salt or with ether and solid carbon dioxide according to the halides in use. The condensed halide passed straight into the reaction bottle, the latter having a protected air exit. The ether was added subsequently. When two gaseous halides were being used together (*e.g.*, methyl chloride and bromide), a two-way tap introduced into the system enabled measurement to be made of each gas independently. The reaction bottle was kept at a suitable temperature during the reaction.

The results obtained are shown below. The meaning of x may be explained by considering a bromide–iodide pair; x_{Br} is the fraction

of 1 mol. of bromide attacked by the metal, so that $(1 - x_{Br})$ mol. of iodide (shown as x_I) is attacked (per 1 mol. of magnesium).

Chloride–bromide pairs.

Radical.	Mixed silver halides (g.).	x_{Br}.	x_{Cl}.	Mean. x_{Br}.	Mean. x_{Cl}.
Methyl	—	—	—	—	—
Ethyl	0·2221	0·772	0·228	0·76	0·24
	0·2210	0·752	0·248		
n-Propyl	0·2263	0·848	0·152	0·81	0·19
	0·2223	0·776	0·224		
n-Butyl	0·1850	0·937	0·063	0·91	0·09
	0·1812	0·878	0·122		

Iodide–chloride pairs.

Radical.	Mixed silver halides (g.).	x_I.	x_{Cl}.	Mean. x_I.	Mean. x_{Cl}.
Methyl	0·2653	0·753	0·247	0·73	0·27
	0·2598	0·705	0·295		
Ethyl	0·2589	0·697	0·303	0·71	0·29
	0·2623	0·727	0·273		
n-Propyl	0·2440	0·570	0·430	0·56	0·44
	0·2410	0·541	0·459		
n-Butyl	0·2409	0·540	0·460	0·54	0·46
	0·2412	0·542	0·458		

Bromide–iodide pairs.

Radical.	Mixed silver halides (g.).	x_{Br}.	x_I.	Mean. x_{Br}.	Mean. x_I.
Methyl	0·2503	0·710	0·290	0·71	0·29
	0·2513	0·718	0·282		
Ethyl	0·2647	0·490	0·510		
	0·2685	0·426	0·575	0·46	0·54
	0·2666	0·458	0·542		
n-Propyl	0·2605	0·562	0·438	0·57	0·43
	0·2601	0·568	0·432		
n-Butyl	0·2764	0·291	0·709	0·27	0·73
	0·2790	0·247	0·753		

Aromatic compounds.

Radical.	Mixed silver halides (g.).	x_{Br}.	x_I.	Mean. x_{Br}.	Mean. x_I.
Phenyl	0·5227	0·505	0·495		
	0·5233	0·542	0·458	0·52	0·48
	0·5244	0·534	0·466		
o-Tolyl	0·2371	0·961	0·039	0·94	0·06
	0·2396	0·916	0·084		
m-Tolyl	0·2400	0·911	0·089		
	0·2431	0·858	0·142	0·88	0·12
	0·2405	0·902	0·098		
p-Tolyl	0·2445	0·834	0·166	0·84	0·16
	0·2440	0·843	0·157		

Benzyl chloride–butyl bromide. By using 0·05 molar quantities, 0·4395 g. and 0·4406 g. of mixed silver halides were obtained in two

experiments, whence x_{Br} is 0·730 and 0·740, respectively, and the mean x_{Br} is 0·73 and x_{Cl} 0·27.

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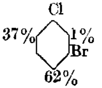
XCIII.—*The Nitration of Mixed* m-*Dihalogenobenzenes.*

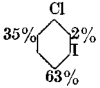
By HORACE ALFRED MAYES and EUSTACE EBENEZER TURNER.

WHEN this investigation was begun, it was hoped to make a complete study of the mononitration of the *m*- and *p*- mixed dihalogenobenzenes, but experiments on the nitration of *p*-halogenoiodobenzenes carried out in conjunction with Mr. C. R. Pinnell have shown that a direct comparison of such compounds is impracticable, owing to the readiness with which the iodine is expelled. This part of our work has been confirmed by van Hove (*Bull. Acad. roy. Belg.*, 1926, **12**, 801, 823).

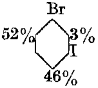
We have, however, made a thorough investigation of the mononitration of three mixed dihalogenobenzenes, with the results indicated by (I), (II) and (III):



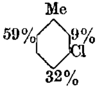
(I.)



(II.)



(III.)



(IV.)

These results are interesting in comparison with those of Holleman and his co-workers (*Rec. trav. chim.*, 1900, **19**, 188, 364; 1905, **24**, 146; 1913, **32**, 134). Holleman showed that, under similar conditions, chloro-, bromo-, and iodo-benzene gave 69·9% and 29·8%, 62·1% and 37·6%, and 58·7% and 41·1% of *p*- and *o*-nitro-derivatives, respectively. The ratio of ortho to para nitration for chlorine, bromine, and iodine in these compounds is therefore 0·43, 0·61 and 0·70, or roughly 6 : 9 : 10. Our nitrations fall fairly well into line with Holleman's results. For instance, when *m*-bromoiodobenzene is nitrated, since both halogens have an approximately equal ortho-para directive ratio, nitration occurs to almost the same extent in positions 4 and 6 (III). The nitration of the other two compounds (I and II) illustrates the same point, for bromine and iodine produce almost precisely the same effect when present in the meta-position to a chlorine atom.

It should be noted that the para-selecting volume effect of the iodine atom must be quite small. This follows equally from Holleman's results and from our own.

Our mononitro-mixtures were analysed by means of the mixed-freezing-point curves and we resorted to common practice to overcome the difficulties due to the presence of a small amount of the 2-nitro-compound. The mononitration of *m*-dichloro- and of *m*-dibromo-benzene produces 4% and 4·6%, respectively, of the 2-nitro-compound (Holleman and Reiding, *Rec. trav. chim.*, 1904, **23**, 359; Holleman, *ibid.*, 1906, **25**, 187).

Wibaut (*ibid.*, 1913, **32**, 244) obtained results for the mononitration of *m*-chlorotoluene as shown in (IV). Now Holleman (*Proc. K. Wetensch. Amsterdam*, 1908, **11**, 248; *Rec. trav. chim.*, 1909, **28**, 408) showed that the ratio of ortho to para nitration of toluene (under conditions similar to those used by Wibaut and by ourselves) was 56·0 : 40·9, *i.e.*, 1·37 : 1. Comparing (IV) with (III), it is perhaps surprising that only 59% nitration occurs in position 6.

We have discovered a minor point which is somewhat difficult to explain. Körner, the only other worker to describe the nitration of mixed *m*-dihalogenobenzenes, found that 1-chloro-3-bromobenzene yielded the 4- and 6-nitro-derivatives and that 1-chloro-3-iodobenzene yielded the 4-derivative and another, undefined compound (*Gazzetta*, 1874, **4**, 379). On the other hand, he stated that 1-bromo-3-iodobenzene on nitration gave two mononitro-derivatives, one of which (no m. p. given) he thought might be the 2-nitro-compound. The second compound, m. p. 126·8°, he regarded as 1-bromo-3-iodo-6-nitrobenzene, and described it as being convertible by alcoholic ammonia into 5-iodo-2-nitroaniline, also obtained by the action of the same reagent on 1 : 3-di-iodo-4-nitrobenzene. We have shown conclusively, however, that Körner's compound, m. p. 126·8°, must be 1-bromo-3-iodo-4 : 6-dinitrobenzene, and that authentic 1-*bromo*-3-*iodo*-6-*nitrobenzene* melts at 76—76·5°.

EXPERIMENTAL.

Preparation of Materials required for plotting the Freezing-point Curves of the Mixtures.—The three *m*-dihalogenobenzenes were prepared from *m*-chloro- and *m*-bromo-aniline and had the b. p.'s given in the literature.

3-Chloro-6-nitroaniline was prepared from *m*-chloroacetanilide by sulphonation, nitration, and removal of the sulpho-group according to D.R.-P. 206,345. A similar method was used successfully for the preparation of 3-bromo-6-nitroaniline.

3-Chloro-4-nitroaniline was prepared by the direct nitration of *m*-chloroacetanilide: under the conditions recorded by Beilstein

and Kurbatow (*Annalen*, 1876, **182**, 94), the nitration mixture occasionally ignited, and even when it did not it gave only a poor yield of the nitro-compound. The following method proved suitable : A solution of *m*-chloroacetanilide (33 g.) in 30 c.c. of glacial acetic acid and 55 c.c. of concentrated sulphuric acid was kept at 10° while 20 c.c. of nitric acid (*d* 1·5) were slowly added, and after 1 hour the mixture was poured on ice. The separated nitro-compound was heated for 1 hour at 100° with excess of 60% sulphuric acid, and the mixture then poured into water; on distillation with steam, 3-chloro-6-nitroaniline passed over (10 g.), leaving a residue (16·5 g.) of almost pure 3-chloro-4-nitroaniline (total yield of mononitro-compounds, 80%).

m-Bromoacetanilide (70 g.) was similarly converted into 17 g. of 3-bromo-6-nitroaniline and 34 g. of 3-bromo-4-nitroaniline.

1-Chloro-3-bromo-6-nitrobenzene was prepared by the Sandmeyer process from 3-bromo-6-nitroaniline. It had setting point 43·4° and m. p. 44·5° (Körner gives 42·4°). 1-Chloro-3-bromo-4-nitrobenzene, from 3-chloro-6-nitroaniline, had setting point 48·4° and melted at 49·5° as stated by Körner.

1-*Chloro*-3-*iodo*-6-*nitrobenzene*, from 3-chloro-4-nitroaniline, had setting point 61·8° and m. p. 63°. Körner probably obtained this compound when he nitrated *m*-chloroiodobenzene, but he gave no m. p. 1-Chloro-3-iodo-4-nitrobenzene, from 3-chloro-6-nitroaniline (obtained by more than one process), had setting point 60·3°; it melted at 61·5° even after repeated crystallisation (Körner gives m. p. 63·4°).

1-*Bromo*-3-*iodo*-6-*nitrobenzene*, from 3-bromo-4-nitroaniline, had setting point 74·4° and melted at 76—76·5° (Found : AgBr + AgI, 0·2544 g.; *M*, in camphor, 322. $C_6H_3O_2NBrI$ requires AgBr + AgI, 0·2531 g.; *M*, 328). Since Körner gave m. p. 126·8°, two check experiments were made as follows : (*a*) a sample of the 3-bromo-4-nitroaniline used for the preparation was converted into 1-chloro-3-bromo-4-nitrobenzene, identical with the product obtained above from 3-chloro-6-nitroaniline. (*b*) *m*-Bromoiodobenzene was warmed with excess of nitric acid (*d* 1·5) and concentrated sulphuric acid, the cooled solution poured on ice, and the solid so obtained crystallised from alcohol; it melted at 125—127°, and was clearly 1-*bromo*-3-*iodo*-4 : 6-*dinitrobenzene* (Found : AgBr + AgI, 0·2444 g.; *M*, in camphor, 378. $C_6H_2O_4N_2BrI$ requires AgBr + AgI, 0·2430 g.; *M*, 373). When warmed with piperidine, the substance was quantitatively converted into dinitrodipiperidinobenzene, m. p. 130°, identical with a specimen obtained from 1 : 3-dichloro-4 : 6-dinitrobenzene.

1-Bromo-3-iodo-4-nitrobenzene, from 3-bromo-6-nitroaniline, had the m. p. recorded by Körner (83·5°), and setting point 82·1°.

Nitration of the Dihalogenobenzenes.—The halogen compound was slowly added to well-stirred nitric acid (*d* 1·5), kept at − 5°, stirring was continued for ¼ hour, and the solution was then poured on ice. The precipitate was washed and dried in the usual manner. Molecular-weight determinations and analyses were carried out in order to make sure that dinitro-compounds were absent.

Sufficient nitric acid was used to effect complete solution in each case. 5 G. of chlorobromo-, chloroiodo-, and bromoiodo-benzene dissolved respectively in 10·5, 13·3, and 15·5 g. of nitric acid. The bromoiodo-compound dissolves rather slowly, and the fact that Körner warmed the mixture to effect solution no doubt accounts for his obtaining a dinitro-compound.

Freezing Points.—These were determined by means of a standard thermometer graduated in fifths of a degree and capable of being read to tenths. The mixtures of isomerides were melted in a test-tube, which was then immersed in a well-stirred bath kept at a suitable temperature.

Determination of the Compositions of Mixtures of the Nitro-compounds.—Freezing-point curves were determined for a number of known mixtures of the two isomerides produced in each nitration. The curves obtained for the chlorobromo- and chloroiodo-nitro-compounds each showed one well-defined minimum point but no other appreciable inflexion. The curve for the bromoiodonitro-compounds was almost flat in the region corresponding to 75—45% of 1-bromo-3-iodo-6-nitrobenzene. The actual f. p.'s of various mixtures were as follows :

1-Chloro-3-bromo-6-nitrobenzene (A) and 1-chloro-3-bromo-4-nitrobenzene (B).

A, %	100	92·74	85·57	79·53	72·74	67·42
F. p.	43·4°	41·9°	39·9°	38·3°	37·0°	36·1°
A, %	62·25	57·79	54·00			
F. p.	36·8°	37·5°	38·2°			
B, %	100	95·01	89·31	84·26	79·9	76·27
F. p.	48·4°	47·4°	46·2°	45·2°	44·5°	43·7°
B, %	68·12	64·64	61·0	57·42	54·68	
F. p.	42·2°	41·5°	40·6°	39·9°	39·3°	

1-Chloro-3-iodo-6-nitrobenzene (A) and 1-chloro-3-iodo-4-nitro benzene (B).

A, %	100	95·03	90·9	82·39	76·41	70·9
F. p.	61·8°	58·7°	56·4°	51·2°	47·3°	43·5°
A, %	60·59	53·99	49·87	47·64		
F. p.	37·2°	31·3°	30·6°	30·4°		
B, %	100	94·47	90·14	84·42	78·22	71·83
F. p.	60·3°	57·3°	54·8°	51·8°	47·8°	43·3°
B, %	64·64	57·82				
F. p.	38·1°	33·0°				

1-Bromo-3-iodo-6-nitrobenzene (A) and 1-bromo-3-iodo-4-nitrobenzene (B).

A, %	100	94·83	89·14	82·92	77·23	72·26
F. p.	74·4°	73·4°	71·8°	70·1°	69·3°	68·9°
A, %	67·78	64·14	60·28	56·46	52·83	
F. p.	68·8°	68·8°	68·7°	68·5°	68·4°	
B, %	100	93·80	89·26	85·62	81·92	78·71
F. p.	82·1°	80·0°	78·4°	77·4°	75·8°	74·7°
B, %	75·19	71·33	67·6	64·2	59·06	
F. p.	73·5°	72·2°	71·1°	70·0°	68·9°	

The freezing point of each crude, dry nitration product was determined. A known quantity of one of the isomerides was added, and the f. p. again determined. In every case, the second point conformed to the curve constructed with the above figures. In the case of the chlorobromo- and chloroiodo-compounds (experiments IV and V with the former, and III, IV, and V with the latter) sufficient of one isomeride was added to give a f. p. on the other arm of the curve. This gave a second figure with which to calculate the original composition. In both series the composition of the original product corresponded to a point on the arm of the curve plotted when A was added to B, so that the first f. p. gave the amount of B present and the second point gave the amount of A present in the new mixture (*i.e.*, after addition of a known amount of A). Taking the mean of the values obtained, we find that the sum A + B is somewhat less than 100%, indicating almost certainly the presence of a little of the 2-nitro-derivative.

The composition of the nitration product of *m*-bromoiodobenzene corresponded to a point on the flat portion of the curve. Both A and B were therefore added in two different experiments, so as to obtain two freezing points, one on each side of the curve. The f. p. of the original nitro-compound always lay slightly below the lowest point on the curve, indicating the presence of a little of the 2-nitro-derivative. This was confirmed by the values obtained for the proportion of A and B present.

In this method of calculation, the assumption is made that a small quantity of the 2-nitro-derivative causes the same depression of f. p. as an equal quantity of A or of B. The results obtained are as follows :

Nitration of m-*chlorobromobenzene*. *Experiment* I. F. p. of product, 40·9° (Found : AgCl + AgBr, 0·2870 g. ; *M*, in camphor, 235. Calc. for mononitro-mixture : AgCl + AgBr, 0·2854 g. ; *M*, 236·5). Addition of A lowered f. p., and therefore the mixture contained 62·0% of B. When 0·2032 g. of A was added to 2·6020 g. of mixture, the new mixture had f. p. 40·1°, corresponding to 57·5% of B.

Experiment II. F. p. of product, 41·2°, corresponding to 63·5% of B. On addition of 0·1556 g. of B to 1·9492 g. of mixture, the f. p. became 41·8°, corresponding to 66·2% of B. Further addition of B (0·1781 g.) to 2·1048 g. of the second mixture gave a third mixture with f. p. 42·3°, corresponding to 68·9% of B.

Experiment III. F. p. of product, 40·6°, corresponding to 61·0% of B. 0·2075 G. of B added to 1·6656 g. of product. New f. p., 41·6°, corresponding to 65·4% of B.

Experiment IV. F. p. of product, 40·8°, corresponding to 61·5% of B. 0·4690 G. of A added to 0·3025 g. of product. New f. p., 37·6°, corresponding to 75·5% of A in new mixture, *i.e.*, to 37·6% of A in original mixture.

Experiment V. F. p. of product, 40·7°, corresponding to 61·3% of B. 0·5352 G. of A added to 0·5130 g. of product. New f. p., 36·5°, corresponding to 70·0% of A, so that the original mixture contained 36·3% of A.

Mean % of A found : 37·0. Mean % of B found : 61·9. Probably 1% of 2-nitro-derivative.

Nitration of m-*chloroiodobenzene. Experiment* I. F. p. of product, 36·4° (Found : AgCl + AgI, 0·2857 g.; *M*, in camphor, 288. Calc. for mononitro-mixture: AgCl + AgI, 0·2865 g.; *M*, 283·5). Addition of B raised f. p., so that mixture contained 62·5% of B. 0·0522 G. of B added to 0·9310 g. of product. New f. p., 37·7°, corresponding to 64·5% of B.

Experiment II. F. p. of product 36·1°, corresponding to 62·2% of B. 0·1456 G. of B added to 3·075 g. of product. New f. p., 37·3°, corresponding to 64·0% of B.

Experiment III. F. p. of product, 37·2°, corresponding to 63·5% of B. 0·4020 G. of A added to 0·6805 g. of product. New f. p., 35·8°, corresponding to 59·0% of A. Original mixture therefore contained 34·8% of A.

Experiment IV. F. p. of product, 37·2°, corresponding to 63·5% of B. 0·2978 G. of A added to 0·6202 g. of product. New f. p., 33·6°, corresponding to 56·5% of A. Original mixture therefore contained 35·6% of A.

Experiment V. F. p. of product, 36·6°, corresponding to 62·7% of B. 1·3670 G. of A added to 2·3755 g. of product. New f. p., 35·8°, corresponding to 59·0% of A. Original mixture therefore contained 35·3% of A.

Mean % of A found : 35·2. Mean % of B found : 62·9. Probably 2% of 2-nitro-derivative.

Nitration of m-*bromoiodobenzene. Experiment* I. F. p. of product, 68·2° (Found : AgBr + AgI, 0·2635 g.; *M*, in camphor, 320. Calc. for mononitro-mixture : AgBr + AgI, 0·2628 g.; *M*,

328). 1·5896 G. of A added to 1·7300 g. of product. New f. p., 39·1°, corresponding to 75·3% of A. Original mixture therefore contained 52·6% of A.

Experiment II. F. p. of product, 68·0°. 1·0012 G. of B. added to 0·9254 g. of product. New f. p., 73·0°, corresponding to 73·6% of B. Original mixture therefore contained 45·1% of B.

Experiment III. F. p. of product, 68·1°. 1·2375 G. of B added to 0·3745 g. of product. New f. p., 77·8°, corresponding to 87·5% of B. Original mixture therefore contained 46·1% of B.

Experiment IV. F. p. of product, 67·9°. 1·3080 G. of A added to 0·4150 g. of product. New f. p., 71·4°, corresponding to 88·1% of A. Original mixture therefore contained 50·6% of A.

Experiment V. 1·5005 G. of the mixture prepared in experiment III (87·5% of B) was added to 1·5390 g. of the mixture from experiment IV (88·1% of A). New mixture had f. p. 68·2°, and contained 50·8% of A.

Mean % of A found : 51·6. Mean % of B found : 45·6. Probably 3% of 2-nitro-derivative.

One of us is indebted to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

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XCIV.—*Derivatives of* 1 : 3-*Dithiolan and of* 1 : 3-*Dithian.*

By JOHN CHARLES ALEXANDER CHIVERS and SAMUEL SMILES.

IN a previous communication (J., 1926, 1723) it was shown that the reaction of aromatic disulphoxides with substances of the type of ethyl malonate, deoxybenzoin, phloroglucinol, and the naphthols in presence of alkali affords a means of inserting the thioaryl group in these substances. Subsequent experiments, which are now described, have been directed to the behaviour under similar conditions of the substances obtained (Otto, *Ber.*, 1882, **15**, 121; 1886, **19**, 1235; 1887, **20**, 2074; 1892, **25**, 1477) from alkyl halides and aromatic thiolsulphonates. The known reactions of these products (Otto, *loc. cit.*) are similar to those of the aromatic disulphoxides and clearly indicate the presence of the thiolsulphonate structure (*e.g.*, I).

(I.) $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}S{\cdot}C_2H_5$ $\qquad$ $\begin{matrix}CH_3{\cdot}C_6H_4{\cdot}SO_2 \\ Na\end{matrix}\Big|\begin{matrix}SR \\ CH(CO_2Et)_2\end{matrix}$ (II.)

It was therefore expected that these disulphoxides of mixed fatty

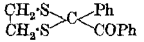
aromatic character would provide a new method of obtaining alkylthiol derivatives of the naphthols, malonic acid, and similar compounds (II). Thioalkyl sulphonates are very easily decomposed by alkali hydroxide and it was found that with this reagent, which was successfully employed in dealing with aromatic thiolsulphonates, none of the required thioalkyl derivatives could be isolated from among the usual products of hydrolysis. When potassium acetate was used to provide the necessary alkaline medium, the desired substitution products were obtained; *e.g.*, dibenzyl disulphoxide yielded with deoxybenzoin the mercaptol of benzil (III), with ethyl malonate, after hydrolysis of the product, benzylthiolacetic acid (IV) was obtained, and β-naphthol and ethylene ditoluene-*p*-thiolsulphonate (V) yielded the ethylene ether of 1-thiol-2-naphthol (VI).

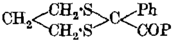
(III.) $(CH_2Ph{\cdot}S)_2CPh{\cdot}COPh$
(IV.) $CH_2Ph{\cdot}S{\cdot}CH_2{\cdot}CO_2H$

$CH_2{\cdot}S{\cdot}SO_2{\cdot}C_6H_4Me$
$CH_2{\cdot}S{\cdot}SO_2{\cdot}C_6H_4Me$ (V.)

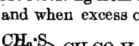
These preliminary results led to the study of the formation of cyclic 1 : 3-dithio-systems from dithiolsulphonates derived from ethane, propane, and pentane (compare V). The behaviour of deoxybenzoin with dibenzyl disulphoxide and aromatic disulphoxides (*loc. cit.*) showed that the dithiol derivatives (*e.g.*, III) are formed even when excess of the ketone is present. Accordingly, this substance readily furnished the cyclic mercaptols of benzil (VII and VIII), but with the αε-pentanedithiolsulphonate no trace of the analogous 8-membered ring was isolated. With ethyl malonate and the aromatic disulphoxides or benzyl disulphoxide, only mono substitution products (*e.g.*, IV) were encountered even when excess o

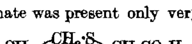
$CH_2{\cdot}S{\cdot}C_{10}H_6{\cdot}OH$
$CH_2{\cdot}S{\cdot}C_{10}H_6{\cdot}OH$
(VI.)


(VII.)


(VIII.)

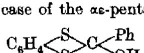
the disulphoxide was present. It is therefore remarkable that th ethane and αγ-propane derivatives gave excellent yields of the cycl compounds resulting from disubstitution of the malonic nucleus (I and X), and when excess of malonate was present only very sma

(IX.) 

 (X.)

quantities of the monosubstituted type (XI) could be detected in t product. On the other hand, in the case of the αε-pentanedithi

(XI.) $CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$
$CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$

 (XII.)

sulphonate no cyclic derivative was formed and only small yiel of the open-chain acid (type XI) were isolated. These resu

clearly indicate the favourable configurations of the 5- and 6-membered rings contained by the 1 : 3-dithiolan and 1 : 3-dithian systems. Although these systems resist fission by mild oxidising agents, being then converted into disulphones (compare Fasbender, *Ber.*, 1888, **21**, 1473; Autenrieth, *Ber.*, 1899, **32**, 1239), they are remarkably sensitive to halogens. In cold acetic acid bromine expels the 2-carbon atom with its substituents and liberates a polymeric sulphide derived from ethane or propane. It seems that this characteristic decomposition is preceded by the formation of an additive product, since the unstable *dibromide* of 1 : 3-*dithiolan*-2-*carboxylic acid* could be isolated under special conditions and the *di-iodides* of this acid and of 1 : 3-*dithian*-2-*carboxylic acid* were also obtained. Oxidation of these acids with hydrogen peroxide led to the unsubstituted disulphones and loss of carbon dioxide; but they were destroyed by cold nitric acid. In the 2-phenyl-1 : 3-benzdithiole series, bromine and nitric acid yield salts (J., 1926, 1823) derived from a pseudo-base (XII), but similar derivatives could not be obtained from the saturated ring-systems now investigated, and no evidence even of their transitory existence during the action of these reagents could be discovered.

EXPERIMENTAL.

Reactions of Benzyl Disulphoxide.—(a) *With deoxybenzoin.* After a solution of the disulphoxide (2 mols.), deoxybenzoin (1 mol.), and potassium acetate (5—6 mols.) in alcohol had been boiled for 6 hours, the solvent was evaporated and the residue rendered alkaline with aqueous sodium carbonate. An ethereal extract of the product contained benzyl disulphide and the monomercaptol of benzil, which could not be satisfactorily separated by the usual means. The latter substance was isolated as the dioxide by treating the crude product with hydrogen peroxide in warm acetic acid. The *dioxide* of the benzyl mercaptol of benzil separated from the cooled reaction mixture in needles, which were purified from alcohol; m. p. 167° (Found: C, 70·7; H, 5·1; *M*, 494. $C_{28}H_{24}O_3S_2$ requires C, 71·1; H, 5·1%; *M*, 472).

(b) *With ethyl malonate.* Interaction of the disulphoxide (1 mol.) and the ester (1·5 mols.) was conducted under conditions similar to those already described. The residue from the ethereal extract was boiled with concentrated hydrochloric acid until hydrolysis was complete. Evaporation of the aqueous acid yielded benzylthiolacetic acid, m. p. 60° (Gabriel, *Ber.*, 1879, **12**, 1641) (Found: C, 59·5; H, 5·4. Calc.: C, 59·3; H, 5·5%).

Reactions of Ethane-αβ-di-p-toluenethiolsulphonate (V).—(a) *With deoxybenzoin.* The interaction of the ketone (2·6 g.) and thiol-

sulphonate (5 g.) in presence of potassium acetate (6 g.) was conducted in boiling alcohol as usual. The residue from the solvent was purified from alcohol; the 2-benzoyl-2-phenyl-1 : 3-dithiolan, m. p. 94—95°, then isolated was identical with the product obtained from αβ-dithiolethane and benzil (Hurtley and Smiles, J., 1926, 2267).

(b) *With ethyl malonate.* Interaction of this ester (5 g.) with the thiolsulphonate (12 g.) in presence of potassium carbonate (8 g.) was effected in boiling alcohol (6 hours). The solvent was removed, and the residue rendered alkaline with sodium carbonate. The portion soluble in ether was boiled with concentrated hydrochloric acid for 8 hours and when the solution obtained was concentrated and cooled, 1 : 3-*dithiolan-2-carboxylic acid* (IX) separated in the crystalline state. From benzene this substance was obtained in prisms, m. p. 90° (Found: C, 32·3; H, 4·3; *M*, 154. $C_4H_6O_2S_2$ requires C, 32·0; H, 4·0%; *M*, 150). The solution from which this material separated after hydrolysis of the ester yielded a small quantity of ethylenedithiolacetic acid (m. p. 107°), showing the characteristic behaviour with cuprous oxide described by Ramberg and Tiberg (*Ber.*, 1914, **47**, 733). When the reaction was carried out in presence of excess of ethyl malonate, the amount of this acid formed was somewhat greater but was always less than that of the cyclic compound. 1 : 3-*Dithiolan-2-carboxylic acid dibromide* was obtained in the crystalline state by cautiously adding bromine to a solution of the acid in low-boiling petroleum. The substance rapidly decomposed, yielding hydrogen bromide, carbon dioxide, and the insoluble ethylene polysulphide, but immediate analysis showed the composition (Found: Br, 50·3. $C_4H_6O_2Br_2S_2$ requires Br, 51·7%). The corresponding *di-iodide* was isolated by adding a little bromine to a solution of the acid (1 mol.) and iodine (2 mols.) in low-boiling petroleum. It was more stable than the bromine derivative, but could not be purified without decomposition (Found: I, 62·3. $C_4H_6O_2I_2S_2$ requires I, 62·8%).

Oxidation of 1 : 3-dithiolan-2-carboxylic acid was effected by excess of hydrogen peroxide in warm acetic acid. After the evolution of carbon dioxide had subsided, the 1 : 3-dithiolan tetroxide separated (yield 50%) from the cooled liquid. It was identified (m. p. 203—204°) in the usual manner and by conversion into the dibromo-derivative (m. p. 271—272°) (Baumann and Walter, *Ber* 1893, **26**, 1129).

*Propane-αγ-di-*p*-toluenethiolsulphonate* (compare V) was prepared from the interaction of αγ-dibromopropane and potassium *p*-tolylthiolsulphonate in boiling alcohol. The viscous material obtained after removal of the solvent solidified when dried an

kept in a vacuum. The required substance separated from a cooled mixture of ethyl acetate and alcohol in needles, m. p. 65—67° (Found: C, 48·6; H, 4·9. $C_{17}H_{20}O_4S_4$ requires C, 49·0; H, 4·8%).

(a) *Reaction with deoxybenzoin.* Interaction of this ketone (4·6 g.) and the thiolsulphonate (12 g.) was conducted as usual in presence of potassium acetate (8 g.). The crude material was purified from alcohol, *2-benzoyl-2-phenyl-*1 : 3-*dithian* (VIII) being obtained in needles, m. p. 99—100° (Found: S, 21·6; *M*, 296. $C_{17}H_{16}OS_2$ requires S, 21·4; *M*, 300).

(b) *Reaction with ethyl malonate.* Reaction of the ester with the thiolsulphonate was effected in presence of potassium acetate in boiling alcohol. The crystalline material obtained after hydrolysis of the crude product with hydrochloric acid was purified from hot water. The resulting 1 : 3-*dithian-2-carboxylic acid* (X) had m. p. 115—116° (Found: C, 36·5; H, 4·8; *M*, 171. $C_5H_8O_2S_2$ requires C, 36·6; H, 4·8%; *M*, 164).

When it was treated with hydrogen peroxide in warm acetic acid, the cyclic disulphone (m. p. 287°) described by Autenrieth and Wolff (*Ber.*, 1899, **32**, 1375) was obtained; it was further identified by conversion into the dibromo-derivative described by these authors. The additive product of this acid with bromine could not be isolated owing to its instability, but the *di-iodo*-derivative was readily obtained in the crystalline state (Found: I, 60·8. $C_5H_8O_2S_2I_2$ requires I, 60·8%).

*Pentane-αε-di-*p*-toluenethiolsulphonate.*—The material obtained in the usual manner from αε-dibromopentane and potassium *p*-tolylthiolsulphonate solidified after remaining 3 weeks in a vacuum. The substance separated from various solvents as a clear, viscous liquid, considered unfit for analysis; it showed the usual reactions of the ethane and propane derivatives already described. Reaction with ethyl malonate was conducted as usual in presence of potassium acetate. After hydrolysis of the product a small amount of *pentane-αε-dithiolacetic acid* (compare XI) was isolated, m. p. 91—92° (Found: C, 42·9; H, 6·6. $C_9H_{16}O_4S_2$ requires C, 42·8; H, 6·3%). This substance was further identified by preparation from αε-dibromopentane and thiolacetic acid. The dibromide (11·5 g.) was slowly added to a boiling solution of thiolacetic acid (9·2 g.) and potassium hydroxide (12 g.) in water (50 c.c.). After 3 hours the solution was cooled and filtered. When 50% sulphuric acid was added to the clear liquid, an almost theoretical yield of the required acid was obtained. This was identical with the product isolated from the interaction of the thiolsulphonate with ethyl malonate; it separated from benzene in fine needles.

In conclusion, we desire to express our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, January 14th*, 1928.]

XCV.—*The Condensation of Certain Aldehydes with Ketones of the Morphine Group.*

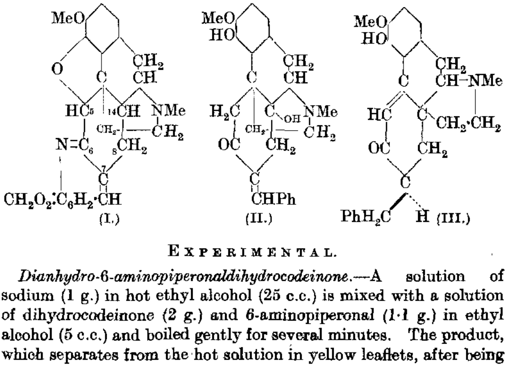
By JOHN MASSON GULLAND.

THE position of the hydroxyl group in hydroxycodeinone and its derivatives (Freund and Speyer, *J. pr. Chem.*, 1916, **94**, 135; Speyer, Selig, and Heil, *Annalen*, 1922, **430**, 1) is an important factor in determining the constitution of thebaine. Gulland and Robinson (*Mem. Manchester Phil. Soc.*, 1925, **69**, No. 10), in showing that the properties of hydroxycodeinone are satisfied only by placing the hydroxyl in position 14, proved that hydroxydihydrocodeinone contains the group $CO{\cdot}CH_2$. One of the steps of this proof consisted in the preparation of dianhydro-6-aminopiperonalhydroxydihydrocodeinone by the condensation of the ketone with 6-aminopiperonal. This quinoline derivative exhibited no fluorescence when dissolved in concentrated sulphuric acid, and thus differed from the simple methylenedioxyquinolines and also from dianhydro-6-aminopiperonalthebainone (Gulland and Robinson, J., 1923, **123**, 998). The absence of this apparently characteristic fluorescence might be considered to weaken the evidence in favour of the presence of a $CO{\cdot}CH_2$ group, but it is now shown that dihydrocodeinone condenses with 6-aminopiperonal, yielding *dianhydro-6-aminopiperonaldihydrocodeinone* (I), which dissolves in concentrated sulphuric acid and in other solvents without exhibiting fluorescence. Dihydrocodeinone undoubtedly contains a $CO{\cdot}CH_2$ group, and it would thus appear that the quinoline bases of this type, in which the attached groups form the larger part of the molecule, do not necessarily yield fluorescent solutions.

The present communication contains also a brief account of a number of experiments which were carried out in the hope of demonstrating, by the preparation of crystalline benzylidene derivatives that the phenolic ketones of the morphine series contain a $CH_2{\cdot}CO{\cdot}CH_2$ group (compare Gulland and Robinson, *ibid.*, pp. 980 998). It may readily be shown that these bases contain one reactive methylene group; for example, *benzylidenehydroxydihydrothebainone* (II) is formed in quantitative yield when hydroxydihydrothebainone (Freund and Speyer, *loc. cit.*) is condensed with benzaldehyde in

alkaline solution. Attempts to show the presence of the second methylene group by the interaction of this benzylidene derivative with 6-aminopiperonal were fruitless, and, as Schöpf has already indicated (*Annalen*, 1927, **452**, 211), this inactivity is comparable with that observed in the case of dehydrocholic acid (Borsche and Frank, *Ber.*, 1924, **57**, 1373) and 3-methyl*cyclo*hexanone (Ruzicka, *Helv. Chim. Acta*, 1926, **9**, 101).

Piperonylidene- and *benzylidene-thebainone* have now been obtained in crystalline condition, and the catalytic reduction of the latter substance yields a mixture of two *benzylthebainones* (III), (A) m. p. 229° and (B) m. p. 179°, which are presumably stereoisomeric about carbon atom 7. These substances are isomeric with, but different from, *benzylidenethebainol*, which is prepared by the condensation of benzaldehyde and thebainol.



(I.) (II.) (III.)

EXPERIMENTAL.

Dianhydro-6-aminopiperonaldihydrocodeinone.—A solution of sodium (1 g.) in hot ethyl alcohol (25 c.c.) is mixed with a solution of dihydrocodeinone (2 g.) and 6-aminopiperonal (1·1 g.) in ethyl alcohol (5 c.c.) and boiled gently for several minutes. The product, which separates from the hot solution in yellow leaflets, after being washed, and dried at 100° (2·2 g.), crystallises from benzene in colourless, rectangular leaflets, m. p. 270—271·5° (Found : C, 73·3 ; H, 5·8. $C_{26}H_{24}O_4N_2$ requires C, 72·9 ; H, 5·6%). It is very sparingly soluble in hot methyl or ethyl alcohol or in ethyl acetate. The solution in concentrated sulphuric acid is colourless and shows no fluorescence. The substance is a non-phenolic base, which contains a methylenedioxy-group, since it responds to Gadamer's test (*Arch. Pharm.*, 1920, **258**, 148).

The *methiodide*, prepared by boiling the base and an excess of methyl iodide in methyl alcohol under reflux for 20 minutes, evaporating the solvent, rubbing the residual yellow gum with hot

ethyl acetate, and grinding the hardened mass with boiling chloroform (the chloroform contains a small quantity of material which was not examined), is obtained, after crystallising twice from methyl alcohol, in pale yellow tablets which become orange at 200°, gradually soften, and decompose finally at about 260° (Found: C, 56·7; H, 4·9. $C_{26}H_{24}O_4N_2$,MeI requires C, 56·8; H, 4·7%).

Benzylidenehydroxydihydrothebainone.—A solution of benzaldehyde (4 g.) and hydroxydihydrothebainone (2·5 g.) in alcoholic potassium hydroxide (25 c.c. of 4%), after being kept at room temperature for 48 hours, is mixed with water, acidified with hydrochloric acid, and extracted with ether. The residual ether having been removed in a current of air, potassium bicarbonate precipitates a small fraction only of the product, which may be crystallised from benzene–ligroin and then from ethyl alcohol. The remainder of the *benzylidene* derivative separates as an oil when the aqueous filtrate is heated on the water-bath for 30 minutes, and solidifies on cooling. It separates from ethyl alcohol in yellow, coarse, pyramidal crystals, m. p. 188° (Found: C, 74·0; H, 6·7. $C_{25}H_{27}O_5N$ requires C, 74·1; H, 6·7%). The colorations developed with concentrated sulphuric acid, concentrated hydrochloric acid, and alcoholic sodium hydroxide are orange-red, very faint yellow, and orange-yellow, respectively. Attempts to prepare a quinoline derivative by condensing the substance with 6-aminopiperonal were fruitless.

Benzylidenethebainone.—A solution of thebainone (Pschorr, Pfaff, and Herrschmann, *Ber.*, 1905, **38**, 3160) (12 g.) and freshly distilled benzaldehyde (16 g.) in ethyl-alcoholic potassium hydroxide (120 c.c. of 5%) is kept in a closed flask at room temperature for 48 hours. The red colour due to the presence of the sodium salt of thebainone changes to a very intense crimson. The solution is poured into water (600 c.c.), just acidified with dilute hydrochloric acid, extracted twice with benzene to remove the excess of benzaldehyde, and neutralised with potassium bicarbonate solution. The flocculent precipitate slowly becomes crystalline, but readily when seeded. After being washed thoroughly with water to remove all traces of bicarbonate, dried on porous tile and then in a vacuum desiccator, it is crystallised from ethyl alcohol, *benzylidenethebainone* being obtained in canary-yellow needles, m. p. 233° (Found: C, 77·7; H, 6·7. $C_{25}H_{25}O_3N$ requires C, 77·5; H, 6·5%). This substance dissolves readily in benzene and chloroform, is insoluble in light petroleum, forms an intense crimson solution in dilute alkali, is easily soluble in organic acids or in dilute mineral acids, yielding yellow solutions, and develops a brilliant green colour with alcoholic ferric chloride. In concentrated hydrochloric or sulphuric acid a deep red colour is produced which is discharged on dilution with water.

The *methiodide* (compare Gulland and Robinson, *loc. cit.*), prepared by warming a suspension of the base (1 g.) in ethyl alcohol (5 c.c.) and methyl iodide (1 c.c.) until it dissolves, separates, on cooling, in fine yellow needles, and recrystallises from ethyl alcohol in the same form, m. p. 195—197° (decomp.) (Found: C, 59·0; H, 5·3. $C_{25}H_{25}O_3N$,MeI requires C, 59·0; H, 5·3%).

Piperonylidenethebainone is prepared from thebainone (2 g.), piperonal (4 g.), and ethyl-alcoholic potassium hydroxide (20 c.c. of 5%) in the manner described in the case of benzylidenethebainone (yield of yellow, semi-crystalline product, 2·7 g.). It is extremely soluble in the usual organic solvents, except ligroin, but it crystallises from a little ethyl alcohol in yellow, wart-like aggregates of crystals, m. p. 176° after drying at 100° (Found: C, 72·1; H, 5·7. $C_{26}H_{25}O_5N$ requires C, 72·4; H, 5·8%). The solution in concentrated hydrochloric or sulphuric acid is intensely reddish-purple and becomes pale yellow on dilution with water.

Reduction of Benzylidenethebainone. The Isomeric Benzylthebainones (A) *and* (B).—A solution of benzylidenethebainone (6·5 g.) in water (80 c.c.) and acetic acid (5 c.c.), when shaken with palladous chloride solution (15 c.c. of 1%) in an atmosphere of hydrogen, absorbs 1 mol. of the gas in about 20 minutes. Absorption then ceases. The palladium is precipitated and removed, and potassium bicarbonate solution added to the filtrate. The colourless, amorphous precipitate produced is dried on porous tile and dissolved in the minimum of boiling alcohol; on cooling, small colourless needles form on the sides of the vessel, and these are collected (A, 0·3 g.) before the appearance of a mass of felted needles, which fill the body of the liquid. The filtrate, after being concentrated, slowly deposits colourless needles or plates (B, 5 g.).

Benzylthebainone (A) is sparingly soluble in alcohol, and separates from this solvent in colourless needles, m. p. 229° (Found: C, 77·0; H, 6·9. $C_{25}H_{27}O_3N$ requires C, 77·1; H, 6·9%). The sodium salt is orange in colour, and the base exhibits an orange halochromic colour in concentrated hydrochloric acid and a bright red in concentrated sulphuric acid. It was recovered unchanged after an attempt to condense it with 6-aminopiperonal in presence of hot ethyl-alcoholic sodium ethoxide.

The *semicarbazone* is formed when a mixture of the base and an excess of semicarbazide hydrochloride and potassium acetate in dilute acetic acid is kept at room temperature over-night. The product is precipitated by ammonia, and after drying, is obtained as a microcrystalline powder, m. p. 155—160°, by repeated precipitation from benzene by means of ligroin (Found: N, 12·2. $C_{26}H_{30}O_3N_4$ requires N, 12·5%).

Benzylthebainone (B) separates from ethyl alcohol in plates, m. p. 179° (Found: C, 76·8; H, 7·0. $C_{25}H_{27}O_3N$ requires C, 77·1; H, 6·9%), or in needles which lose solvent and become pasty at about 110° (Found: loss at 100°, 5·3. Required for ½EtOH, 5·6%. Found in dried material: C, 77·3; H, 7·1%). Each of these forms may be obtained free from the other by utilising the following facts: (i) The plates separate first and pass into the needle form after remaining for some time in contact with the solvent, and (ii) the needles dissolve more rapidly than the plates when a suspension of the two forms is warmed with ethyl alcohol. Both forms of this substance are more soluble than the isomeride (A), and show the same halochromic colours; the sparingly soluble, orange sodium salt separates in needles when a hot slightly alkaline solution is cooled. The base was recovered unchanged after an attempt to condense it with 6-aminopiperonal.

The *semicarbazone*, prepared as described in the case of the isomeride (A), crystallises from dilute ethyl alcohol in needles, m. p. 140—145° (unaltered by further crystallisation) (Found in material dried at 100°; C, 69·0; H, 6·8. $C_{26}H_{30}O_3N_4$ requires C, 69·9; H, 6·8%).

The *oxime*, prepared in a similar manner, is precipitated by sodium carbonate, collected, and dried on porous tile. It becomes crystalline on boiling with ethyl alcohol, and is then collected and recrystallised from the same solvent, from which it separates in colourless columns, m. p. 152° (Found: N, 6·7. $C_{25}H_{28}O_3N_2$ requires N, 6·9%). This oxime is not reduced when a solution in dilute acetic acid is shaken with palladium and hydrogen (compare Speyer, Selig, and Heil, *loc. cit.*).

Benzylidenethebainol.—The condensation of benzaldehyde (3 g.) with thebainol (2 g.) is carried out in the manner described in the case of benzylidenethebainone. *Benzylidenethebainol* crystallises from ethyl alcohol in faintly yellow needles, m. p. 100—102° (Found in material dried at 100°; C, 77·1; H, 7·2. $C_{25}H_{27}O_3N$ requires C, 77·1; H, 6·9%). The solution in concentrated sulphuric acid is orange-red, in concentrated hydrochloric acid yellow, and these colours are discharged on dilution with water. The solution in alcoholic or hot aqueous sodium hydroxide is orange-yellow.

The author wishes to thank Professor Robinson for the interest which he has taken in this work, and acknowledges his indebtedness to the Chemical Society for a grant which has defrayed a part of the cost of the investigation.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, February 3rd, 1928.*]

XCVI.—*Cryoscopic Evidence of Compound Formation in Mixtures of Organic Liquids.*

By Walter Matthew Madgin, John Buttery Peel, and Henry Vincent Aird Briscoe.

Previous work on binary mixtures of non-aqueous liquids has led to the view that in many cases, and especially when the mixture is formed with considerable rise in temperature, the constituents are to some extent associated together in a manner indistinguishable from chemical union (Madgin and Briscoe, *J. Soc. Chem. Ind.*, 1927, **46**, 107T; Madgin, Peel, and Briscoe, J., 1927, 2873). The present paper records attempts to test this view by cryoscopic methods.

Evidently, if freezing-point depressions were strictly proportional to the concentration of the solute, and constant, with a given solvent, for equimolecular proportions of different solutes, the depressions for mixed solutes having no effect on each other should follow the mixture law. If the solutes associate together, the depression for the mixed solutes should be less than that to be expected from the mixture law. This argument has been applied to show that compounds are formed (*a*) between quinoline and ethyl tartrate in ethylene dibromide as solvent (Patterson and Montgomerie, J., 1909, **95**, 1138), and (*b*) between ethyl acetate and acetic or trichloroacetic acid in benzene solution (Kendall and Booge, J., 1925, **127**, 1776).

There is, however, in all such evidence, an intrinsic weakness, explicitly admitted by Patterson and Montgomerie, arising from our ignorance of the mechanism of the depression of the freezing point, and from the fact that, in the concentration usually employed, the observed depressions often deviate considerably from those calculated according to the mixture law.

Cryoscopic determinations of the molecular weights of organic compounds in apparently inert solvents have often given values considerably greater than those corresponding with the accepted formulæ of the solutes; *e.g.*, in the cases of hydroxy-compounds and phenols in benzene and naphthalene (Auwers, *Z. physikal. Chem.*, 1894, **15**, 33; 1895, **18**, 595); alcohols, acids, and phenol in bromoform (Ampola and Manuelli, *Gazzetta*, 1895, **25**, ii, 91); alcohols and phenols in *p*-bromotoluene (Paterno, *ibid.*, 1896, **26**, ii, 1); acetic acid in benzene (Kendall and Booge, *loc. cit.*); alcohols, phenols, and acids in nitrobenzene (Bury, *J. Physical Chem.*, 1926, **30**, 694).

It has frequently been held that an abnormally small depression of the freezing point is evidence that the solute is associated (see *e.g.*, Turner and Pollard, J., 1914, **105**, 1751; Brown and Bury,

loc. cit.), but such effects have also been attributed to the formation of solid solutions of the solvent and solute (Garelli, *Gazzetta*, 1894, **24**, ii, 229) or, more vaguely, to their mutual influence (Auwers, *Z. physikal. Chem.*, 1899, **30**, 300).

In general, the abnormalities in freezing-point depressions increase with the concentration of the solute (see, *e.g.*, Ampola and Manuelli, and Brown and Bury, *locc. cit.*), but Paternò (*Gazzetta*, 1896, **26**, ii, 363) has found that, with phenol as the solvent, several solutes give depressions that become less abnormal as the concentration increases. Ethyl alcohol as a solute has often been found to behave very abnormally; thus, the molecular weight for this alcohol in benzene (Auwers, *loc. cit.*) was seven times, and in bromoform (Ampola and Manuelli, *loc. cit.*) nine times that corresponding with the simple formula. We have confirmed the general trend of these results with ethyl alcohol in both benzene and nitrobenzene as solvents, as is shown by the following data:

Solvent.	Benzene.	Nitrobenzene.
Range of composition of solutions (weight of ethyl alcohol)	5·0—0·5%	4·6—0·2%
Range of variation of molecular weight ($C_2H_5{\cdot}OH = 46$)	*130—62*	*108—55*

Without entering into a discussion of these curious results, it is obvious that any attempt to obtain evidence of compound formation between solutes must be subject to grave uncertainty if based merely on calculation. We have sought, therefore, to apply the cryoscopic test for compound formation in such a manner that the result is obtained directly and without any calculation whatever. Whereas previous workers have proceeded by adding one solute to a solution of the other, we, in investigating each pair of liquids, have dissolved them separately in a given solvent to give solutions having the *same depression* of the freezing point: these solutions have then been mixed, and the depression has been determined for the mixed solutions.

The selection of liquid pairs for investigation was based upon the previous survey of the temperature change produced on mixing in equal volumes 628 pairs among 37 liquids (Madgin and Briscoe, *loc. cit.*). In an extended study of compound formation in pairs of organic liquids, Bramley (J., 1916, **109**, 10, 434, 469, 496) found that a marked rise of temperature accompanied the mixing of liquids in those cases where it was probable, on other grounds, that compounds were formed, and his results show that *o*-chlorophenol forms compounds of considerable stability with both pyridine and aniline. The pairs of liquids investigated therefore comprise these two pairs (for comparison), several other pairs which give a rise of temperature

on mixing, though there is no other reason to suspect compound formatiou, and also a few pairs where the thermal effect of mixing is negative.

The experimental procedure calls for little description. Freezing points were determined in a standard Beckmann apparatus, with all usual precautions and with a thermometer divided to 0·01°. Solutions of the two solutes in a solvent were made of approximately the desired strength by using calculated quantities, and then adjusted by trial until both gave substantially the same depression of freezing point. As soon as these depressions had been finally determined, the solutions were transferred to stoppered flasks and, with the least possible delay, equal volumes were mixed and the freezing point of the mixture was determined.

Three solvents were used: benzene, nitrobenzene, and bromoform: the concentration of the solutions was of the order of 0·05 molar fraction of solute, and the data recorded are in every case the mean of at least three closely concordant observations. The results are in Table I, the columns of which show (I) the serial number of the experiment, (II) the constituents A and B of the mixture, (III) the solvent, (IV and V) the depressions for A and B separately, (VI) the depression for the mixed solutions of A and B, (VII) the alteration of freezing point produced by mixing, and (VIII) the temperature change produced on mixing equal volumes of the pure liquids A and B (Madgin and Briscoe, *loc. cit.*). The data in column (VII) are, in effect, a measure of the deviation from the simple mixture law and are accordingly marked + and −.

On examining the table it is at once evident that in many cases the depressions for mixtures, Δ_{A+B}, are markedly less than those, Δ_A and Δ_B, for the constituent solutions. This is so in experiments 1—8 inclusive, and 11, 12, 13, and 15. As this effect is identical with that produced by diminishing the concentration of either solute singly in its solution, it appears to prove quite definitely and irrespective of any calculation that in the mixed solutions the effective molecular concentration of the solutes has been diminished, and hence that association of the two solutes with each other has occurred. Association of either solute with the solvent or dissociation of complex molecules of either solute (both of which might occur, for on mixing the solutions the concentration of solution with respect to either solute is halved) would, in effect, increase the concentration of the solute, and would tend to produce a greater depression of the freezing point (see, *e.g.*, Jones and Chambers, *Amer. Chem. J.*, 1900, **23**, 89). Hence the data prove that compounds are formed in solution by *o*-chlorophenol with pyridine, aniline, or ether; by chloroform with ether or acetone; and by bromoform with acetone.

TABLE I.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
			Δ_A.	Δ_B.	Δ_{A+B}.		
1	A. *o*-Chlorophenol	Y	1·985	2·005	1·590	−0·405	
2	B. Pyridine	X	2·018	2·027	1·791	−0·232	
3	A. *o*-Chlorophenol	Y	1·990	1·985	1·945	−0·042	+13·85°
4	B. Aniline	X	1·990	2·030	1·940	−0·07	
5	A. *o*-Chlorophenol	Y	2·070	2·070	1·950	−0·12	+21·5
6	B. Ether	X	2·045	2·040	1·915	−0·127	
7	A. Ether	X	2·040	2·030	2·000	−0·03	+14·2
8	B. Chloroform	Y	2·015	2·018	1·975	−0·042	
9	A. Chloroform	X	2·030	2·020	2·030	+0·005	+12·65
10	B. Acetone	X	2·040	2·018	2·030	+0·006	
11		Y	2·018	2·030	1·085	−0·039	
12	A. Acetone	X	2·020	2·030	2·005	−0·02	+ 8·3
13	B. Bromoform	Y	2·020	2·030	2·015	−0·01	
14	A. Acetone	X	2·020	2·025	2·020	−0·0025	− 9·75
15	B. Carbon disulphide	Y	2·020	2·025	1·990	−0·033	
16	A. Carbon disulphide	X	2·025	2·025	2·030	+0·005	− 8·5
17	B. Aniline	Y	2·010	2·015	2·015	+0·003	
18	A. Chloroform	X	2·000	2·005	2·000	−0·0025	− 4·4
19	B. Carbon disulphide	Y	1·755	1·750	1·740	−0·013	
20	A. Chloroform	X	2·000	2·025	2·020	+0·008	− 1·0
21	B. Aniline	Y	2·018	2·025	2·020	−0·002	
22	A. Ether	X	2·020	2·025	2·025	+0·002	+ 3·1
23	B. Aniline	Y	1·980	1·990	1·990	+0·005	
24	A. Ethyl acetate B. Methyl acetate	X	2·015	2·025	2·020	0	− 0·05
25	A. Ethyl acetate B. Ether	X	2·015	2·010	2·010	−0·002	− 1·2
26	A. Methyl acetate B. Ether	X	2·025	2·010	2·020	+0·002	− 2·3
27	A. Methyl acetate B. Aniline	X	2·025	2·025	2·025	0	+ 3·15
28	A. Ethyl alcohol	X	1·990	2·005	2·230	+0·233	+ 3·95
29	B. Chloroform	X	2·018	2·020	2·268	+0·25	
30		Y	1·918	1·930	2·045	+0·121	
31		Z	1·960	1·970	2·100	+0·135	

Solvents. X = Benzene. Y = Nitrobenzene. Z = Bromoform.

If confirmation of this view were needed it is to be found in Bramley's evidence (*loc. cit.*) that *o*-chlorophenol forms definite compounds with pyridine and aniline: evidently these compounds persist to some extent in solution. Recently, also, a study of the turbulent streaming of liquids has afforded evidence that acetone–chloroform mixtures contain a compound (Kremann, Springer, and Roth, *Z. physikal. Chem.*, 1927, **130**, 415).

It is noticeable that in Expt. 2 Δ_{A+B} differs less from Δ_A or Δ_B than in Expt. 1. Thus, apparently, nitrobenzene as solvent is less effective than benzene in causing dissociation of the *o*-chlorophenol–pyridine compound. Other examples of such differences in the

effect of different solvents are to be found, notably in Expts. 9, 10, and 11 for chloroform-acetone, and in Expts. 14 and 15 for acetone-carbon disulphide. With regard to the latter pair, indeed, it appears that the compound which evidently exists in nitrobenzene solution is practically completely dissociated in benzene solution. There are also cases, *e.g.*, Expts. 3 and 4, where apparently nitrobenzene is the solvent which is more effective in causing dissociation.

Expts. 28—31 inclusive are remarkable in that the depression for the mixture is greater than that for the constituents, but this curious effect may readily be explained by reference to the behaviour of ethyl alcohol referred to above. It appears probable that the effect of dissociation of complex alcohol molecules outweighs any effect due to compound formation between alcohol and chloroform. Expt. 15 may show that compound formation can occur in certain solvents between solutes whose admixture in the pure state is attended by a substantial fall in temperature, but, evidently, no generalisation can safely be based on a single instance of this kind.

The essential point which emerges clearly from the experiments here reported is that in the liquid pairs involved in Expts. 1—13 inclusive, admixture of the pure liquids is attended by a considerable rise of temperature. Thus our earlier view, that in general such a rise of temperature is evidence of compound formation, is confirmed.

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XCVII.—*The Adsorption of Hydrogen Ions and Its Effect on the Swelling and Electrical Charge of Gelatin.*

By BHUPENDRA NATH GHOSH.

IT is well known that gelatin swells more in dilute solutions of acids than in pure water. At p_H 4·8 the swelling is generally a minimum, but it increases with the decrease in p_H, reaches a maximum and then diminishes again. Several theories have been advanced to explain this behaviour.

(1) In acid solutions the particles of the gel adsorb hydrogen ions which impart a positive charge to them. The similarly charged particles repel one another and thereby cause the swelling. At high concentrations of acids, the negative ions tend more and more to

neutralise the electrical charge and so decrease the swelling. This theory was supported by Tolman and Stearn (*J. Amer. Chem. Soc.*, 1918, **40**, 264), who observed that the swelling of blood fibrin and also of gelatin is much greater in solutions of nitric and hydrochloric acids than of sulphuric acid at the same p_H; the presence of salts in high concentrations also depressed the swelling. They therefore suggest that the SO''_4 ion, because of its bivalent nature, has a much greater effect in neutralising the positive charge, and therefore decreasing the swelling, than the univalent Cl' or NO'_3 ions. Similarly, in presence of salts, the high anion concentration decreases the charge and hence the swelling.

(2) Pauli, Hardy, Loeb and others have suggested that the protein ions are more heavily hydrated than their neutral molecules. According to Pauli (*Biochem. Z.*, 1909, **18**, 368) and Fischer ("Œdema and Nephritis," 1921, pp. 145—151), hydration is responsible for swelling. The increase in volume of gelatin may therefore be due to a greater hydration of its particles with increasing electrical charge.

(3) Gelatin combines with acids forming salts, the kations of which are non-diffusible. This, according to Donnan's principle of membrane equilibrium, brings about a greater concentration and hence greater osmotic pressure of the diffusible ions inside the gel than in the outside solution, and so causes it to swell. This theory was put forward by Procter and Wilson (J., 1916, **109**, 307), and subsequently Wilson and Wilson (*J. Amer. Chem. Soc.*, 1918, **40**, 886) derived an equation connecting swelling with the concentration of a univalent kation inside the gel. The equation agrees fairly with experimental results (compare R. H. Bogue, "The Theory and Application of Colloidal Behaviour," Vol. I, p. 12).

If there be any relation between electrical charge and swelling, they should run parallel to each other. With increasing concentration of hydrogen ions both the electrical charge and the swelling should increase, reach a maximum, and then diminish; also, at the same p_H the electrical charge in solutions of sulphuric acid should be less than in those of hydrochloric or nitric acid. The above considerations should also apply to the case where swelling is attributed to the greater hydration of the gel particles with their increasing electrical charge. A relation is also to be expected between the amounts of hydrogen ion adsorbed and the surface density of the electrical charge, since the latter originates from the adsorption of hydrogen ions. A simultaneous measurement of swelling, electrical charge, and adsorption of hydrogen ions on the same sample of gelatin, was therefore undertaken in order to decide whether there is any relation between the three quantities.

EXPERIMENTAL.

The powdered gelatin was purified by repeated washing with dilute acetic acid at 10° (Loeb, *J. Gen. Physiol.*, 1918, **1**, 45). It was then washed with cold distilled water at 5°, dehydrated by washing with absolute alcohol, and dried in a current of air. The dried sample contained 16·7% water and had an ash content of 0·12%. 0·8 G. portions were placed in two Pyrex-glass beakers and covered with 200 c.c. of the acid solution. The beakers were placed in a thermostat at 17° and their contents stirred from time to time. After 24 hours, the gelatin from one of the beakers was transferred to a filter-paper, drained thoroughly, washed with 20 c.c. of distilled water, again drained, and pressed lightly between filter papers to remove as much liquid as possible. It was then transferred to a measuring cylinder and melted by warming on a water-bath at about 40°. The p_H of the melted gel was measured by the *E.M.F.* method. The p_H of the acid solution before and after adsorption was also measured by the same method, and the amount of acid adsorbed by gelatin, α, calculated in the following way.

Let V_1 be the original volume of the acid solution, V_2 its final volume and V the volume of water imbibed by the gelatin. Also let C_1 and C_2 be the initial and final concentration of hydrogen ions in the solution and C_3 the concentration of free hydrogen ions inside the gel. Then

$$\alpha = V_1C_1 - V_2C_2 - VC_3 \quad . \quad . \quad . \quad . \quad (1)$$

But, neglecting the slight change in the total volume of the solution and gelatin, we have $V_2 = V_1 - V$, and substitution in (1) then gives $\alpha = V_1C_1 - (V_1 - V)C_2 - VC_3 = V_1(C_1 - C_2) + V(C_2 - C_3)$.

In applying this equation, V is taken to be equal to the volume of the melted gels; any slight error thus introduced causes a relatively much smaller error in α.

The gelatin contained in the second beaker was transferred to a measuring cylinder and allowed to settle in the thermostat for 3 hours. The volume was noted. The substance was then removed on a filter-paper, and washed two or three times with a solution having the same p_H as the melted gel. It was again transferred to the measuring cylinder and melted by warming to about 40°; a few c.c. of acid solution of the same p_H as the gel were added to make the total volume always 26 c.c., and 23 c.c. of this were transferred to a U-tube and allowed to set for 24 hours.

The electroendosmotic method was used to measure the variation of electrical charge with hydrogen-ion concentration. The arrangement was an improvement on that previously described by the

author (J., 1926, 2605), in that a definite potential (indicated by a voltmeter) was applied between the electrodes. The potential could be maintained constant within ± 1 volt by means of an adjustable resistance. The potential across the diaphragm was determined in the following way. The total resistance between the electrodes, consisting of the diaphragm and the acid solution, was measured by the conductivity method. The electrodes were then lowered so as just to touch the diaphragm, and the resistance was measured again. If T and D be the total and the diaphragm resistances, respectively, then the potential across the diaphragm is given by the expression DE/T, where E is the potential indicated by the voltmeter when the electrodes were in their original position (*i.e.*, when the total resistance between them was T). In order to maintain a constant potential across the diaphragm, it is necessary that E as well as the ratio D/T should remain constant. E was kept constant during the experiment by means of the adjustable resistance, and resistances D and T, as measured immediately before and after the experiment, always showed a variation of less than 3% in D/T. The mean was used in calculating the potential across the diaphragm. The U-tube was always filled with a solution having the same p_H as the gel constituting the diaphragm immediately before the experiment, which lasted about ½ hour. The electroendosmotic experiments were carried out at 16°. The distance moved by the air bubble in a definite time at constant potential gradient across the diaphragm is proportional to the surface density of the electrical charge of the gel, which was found to be zero at p_H 4·8—5·0. The results are in the table.

$(p_H)_1$, $(p_H)_2$, and $(p_H)_g$ respectively represent the p_H of the solution before and after adsorption, and of the melted gel; α is given in terms of c.c. of N-acid adsorbed; "Vol." is the volume (in c.c.) of the gel; V the approximate volume of the melted gel; and β the velocity of the air bubble in cm. per min.

In the above experiments the potential across the diaphragm was maintained constant at 80 volts. The calculated values of α were derived from the formula $\alpha = K_3x/(1 + K_4x)$ (see p. 717), where K_3 and K_4 are constants and x is the concentration of hydrogen ions inside the gel. For hydrochloric, nitric, and trichloroacetic acids, the values of K_3 and K_4 used were 1240 and 1800, respectively. They are somewhat different in the case of sulphuric acid, *viz.*, $K_3 = 1420$ and $K_4 = 2240$. All the acids have been assumed to be completely dissociated within the range of concentrations investigated. If the low value of the dissociation of sulphuric acid be taken into consideration, the amount of adsorption will be a little higher than that given in the table.

$(p_H)_1$.	$(p_H)_2$.	$(p_H)_g$.	α, Found.	α, Calc.	Vol.	V.	β.	β/α.
			Hydrochloric acid.					
1·81	1·89	2·17	0·64*	0·63	29	20	0·81	1·27
2·02	2·14	2·52	0·55	0·58	31	21	0·68	1·24
2·10	2·24	2·70	0·52	0·54	32·5	22	0·63	1·25
2·40	2·62	3·22	0·36*	0·36	35	24	0·47	1·30
2·68	2·99	3·60	0·24	0·22	27·5	20·5	0·33	1·37
			Nitric acid.					
1·82	1·90	2·19	0·63	0·63	29	20·5	0·79	1·25
1·94	2·04	2·38	0·58	0·60	30·5	21	0·70	1·21
2·09	2·22	2·68	0·57	0·54	32	22·5	0·63	1·23
2·42	2·66	3·23	0·36	0·36	34·5	24	0·50	1·39
2·72	3·05	3·62	0·23	0·22	27·5	20	0·31	1·35
			Trichloroacetic acid.					
1·77	1·84	2·10	0·64	0·64	28·5	19·5	0·80	1·25
1·92	2·02	2·38	0·60	0·60	30·5	21	0·72	1·20
2·07	2·20	2·68	0·53	0·54	32	22	0·65	1·23
2·34	2·53	3·19	0·38	0·37	34	24	0·54	1·31
2·67	2·99	3·60	0·24	0·22	27	21·5	0·33	1·37
			Sulphuric acid.					
1·77	1·84	2·10	0·60*	0·60	15	13	0·62	1·03
1·88	1·97	2·30	0·57	0·58	16	14	0·59	1·03
2·12	2·26	2·74	0·47	0·50	18·5	15	0·55	1·17
2·36	2·55	3·26	0·33*	0·35	20·5	16·5	0·46	1·31
2·60	2·90	3·58	0·25	0·23	16·5	14	0·34	1·37

* The values thus marked were used in calculating K_3 and K_4 (see p. 717).

Discussion.

It will be seen from the above table that, at first, with increasing concentration of hydrogen ion the swelling, electrical charge, and adsorption of hydrogen ions, all increase. At a certain p_H (about 2·6) the swelling reaches its maximum value and then begins to diminish, whilst the electrical charge and adsorption of hydrogen ions continue to increase. Had the swelling been due to the electrostatic repulsion between the similarly charged particles of the gel, it could *not have diminished so long as the electrical charge was increasing.* With sulphuric acid, swelling and electrical charge are both less than with hydrochloric, nitric, and trichloroacetic acids, but this fact alone does not justify one in inferring any relation between them. Here also, as with the other acids, we observe that whilst the electrical charge continues to increase with diminishing p_H, the swelling attains its maximum value at about p_H 2·6 and then decreases. Furthermore, at low hydrogen-ion concentration the electrical charge with sulphuric acid is the same as with the other acids, whilst the swelling is distinctly less. The above results therefore lead definitely to the conclusion that there is no relation between electrical charge and swelling in the case of gelatin. For the same reasons the

swelling of gelatin in acid solutions cannot be due to the increasing hydration of its particles with increasing electrical charge.

It has already been mentioned that as the adsorption of hydrogen ions imparts a positive charge to the gel there should be a close relation between the two. It will appear from the above results that there is a direct proportionality between the surface density of electrical charge and the amount of hydrogen ions adsorbed. The *ratio* (β/α) *of the distance moved by the air bubble to the amount* of hydrogen ions adsorbed is, within the range investigated, approximately constant for the first three acids, indicating that only few univalent anions are electrically adsorbed. This is possible when the thickness of the electrically adsorbed layer is great (compare Mukherjee, Faraday Soc. Discussion, 1920—1921, **16**, Appendix, p. 105). With increasing surface density of electrical charge, however, the electrical attraction on the anions will increase more and more, and so at high concentrations the number of anions electrically adsorbed will become appreciable and the ratio β/α will tend to decrease. This will be observed in the case of sulphuric acid. At low hydrogen-ion concentrations the ratio is almost the same as with the other acids (about 1·35), but as the concentration of sulphuric acid increases, the ratio gradually decreases. The SO_4'' ion carries two units of electrical charge and hence the force tending to bind it to the surface is much greater than in the case of the univalent anions.

There are different views regarding the interaction of acids with gelatin. Some, *e.g.*, Procter and Wilson, hold that acids combine chemically with gelatin forming salts of the type GHA, where GH represents the kation and A the anion. Many others, however, consider the process as one of adsorption (Wilson and Wilson, *loc cit.*). *It is difficult to believe that the colloid particles in the sol and gel of* gelatin are molecules and not aggregates of a large number of molecules. The so-called molecular weight of gelatin, as obtained by different workers, varies from 10,000 to 20,000 or more. A molecular weight much smaller than this would generally give a particle of colloidal size, with a large solid–liquid interface. Besides the molecular weight, other properties of gelatin vary with its source and its previous treatment. Recently Kraemer and Dexter (*J. Physical Chem.*, 1927, **31**, 764) have observed that even the isoelectric point of gelatin, as revealed by measurements on the scattering of light, varies with its origin. Kruyt and Tendeloo (*ibid.*, 1925, **29**, 1303) have shown that ions other than hydrogen, such as ferrocyanide, affect the viscosity and electrical charge of gelatin. In such cases the same valency effects of the ions make themselves felt as are observed with the hydrophobic colloids. In view of these

facts, it is better to consider the interaction of gelatin with hydrogen ions as one of adsorption. Rinde (*Phil. Mag.*, 1926, **1**, 32) has shown from Loeb's data that the amount of hydrogen ions adsorbed by gelatin can be calculated with fair accuracy from an equation similar to that which gave satisfactory results in the present instance (see tables and below).

It will now be shown that the assumption that hydrogen ions are adsorbed by gelatin also leads to the derivation of an equation for swelling similar to that obtained by Wilson and Wilson (*loc. cit.*).

Let it be assumed that 1 g. of gelatin is immersed in a dilute solution of hydrochloric acid and sufficient time allowed for the attainment of equilibrium. If N be the total number of active points on the surface of the gel, the rate at which hydrogen ions are adsorbed $= K_1N(1 - \theta)x$, where x is the equilibrium concentration of hydrogen ions inside the gel, θ the fraction of the total surface covered, and K_1 a constant. The rate at which these ions escape from the surface $= K_2N\theta$. When equilibrium is attained we have (compare Langmuir's equations)

$$K_1N(1 - \theta)x = K_2N\theta$$

or $$xN = N\theta(x + K_0) \quad \ldots \ldots \ldots \quad (2)$$

where $K_0 = K_2/K_1$, or, putting $N/K_0 = K_3$, and $1/K_0 = K_4$,

$$N\theta = K_3x/(1 + K_4x) \quad \ldots \ldots \ldots \quad (3)\ *$$

Corresponding to the $N\theta$ hydrogen ions adsorbed there must be in the neigbbourhood of the surface an equal number of chlorine ions, of which a fraction a may be electrically adsorbed. The number of free anions is then equal to $(1 - a)N\theta$. The value of a, however, depends on the coneentration of the chlorine ions and also on the thickness of the double layer (compare Mukherjee, *loc. cit.*). The electroendosmotic experiments show that a is negligible in the case of hydrochloric, nitric, and trichloroacetic acids below about 0·02 normal. These free anions should behave normally so far as their activity is concerned. The concentration of free chlorine ions inside the gel $= N\theta(1 - a)/(V + V_0)$ where V_0 is the initial volume and V the increase in volume of the gel (see p. 713). The equilibrium concentration of hydrogen ions inside the gel is x, and corresponding to this we have a concentration x of chlorine ions in the gel. Hence the concentration of total chlorine ions inside the gel $= N\theta(1 - a)/(V + V_0) + x$. If y be the equilibrium concentration of hydrogen

* This formula was used in the calculation of the adsorption of hydrogen ons (see tables on p. 715).

ıd chlorine ions outside the gel, we have from Donnan's principle membrane equilibrium

$$\left[\frac{N\theta(1-a)}{(V+V_0)}+x\right].x=y^2 \quad . \quad . \quad . \quad . \quad (4)$$

; follows mathematically from this that the total concentration of ›ns *inside the gel is greater than that in the surrounding solution.* f e denotes this excess then

$$e=2x+\frac{N\theta(1-a)}{(V+V_0)}-2y \quad . \quad . \quad . \quad . \quad (5)$$

'rom (4) and (5) we get

$$y=x+\sqrt{ex} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

ınd from (5) and (6)

$$N\theta(1-a)/(V+V_0)=e+2\sqrt{ex} \quad . \quad . \quad . \quad (7)$$

As the concentration of ions inside the gel is greater than that outside, the osmotic pressure inside will be greater, and so the gel tends to swell.

It is now assumed that $e=HV$, where H is a constant containing the modulus of bulk elasticity (compare Wilson and Wilson, *loc. cit.*, and Scarth, *J. Physical Chem.*, 1925, **29**, 1019). Substituting this value of e in (7) we have

$$N\theta=(V+V_0)(HV+2\sqrt{HVx})/(1-a) \quad . \quad . \quad (8)$$

Putting the above value of $N\theta$ in (2), and neglecting V_0, since it is small compared with V, we obtain

$$V(K_0+x)(HV+2\sqrt{HVx})=xN(1-a) \quad . \quad . \quad (9)$$

It has already been mentioned that a is negligible at low concentrations of the monobasic acids, so equation (9) reduces to the form

$$V(K_0+x)(HV+2\sqrt{HVx})=xN \quad . \quad . \quad . \quad (10)$$

The equation obtained by Wilson and Wilson, when one starts with 1 g. and not 1 millimol. of gelatin, assumes the form

$$MV(K_0+x)(HV+2\sqrt{HVx})=x$$

where M is the molecular weight of gelatin, and thus resembles (10).

In deducing their equation, Wilson and Wilson had to assume (1) that the active mass of gelatin is equal to the number of g. mols. of gelatin divided by the volume of the gel, and (2) that the kation of the salt GHA does not exert any osmotic pressure (compare Procter, Faraday Soc. Discussion, 1920—1921, **16**, Appendix, p. 41). These assumptions do not enter into the deduction of equation (10); moreover, the value of M for gelatin is uncertain. The value of N

in equation (10) is given by the maximum number of hydrogen ions which 1 g. of gelatin can adsorb and may be easily determined experimentally for any particular sample.

It follows from equation (9) that when x is constant any factor *which will tend to increase* (a) *will decrease the swelling.* The depression in swelling caused by the addition of alcohol and similar substances is probably due to a diminution in the dielectric constant of the medium. This will tend to increase (a) and hence depress the swelling.

Summary.

(1) Simultaneous measurements of electrical charge and swelling at different values of p_H indicate that electrostatic repulsion between the similarly charged particles of the gel cannot be the cause of the swelling. They also show that swelling is not due to the increasing hydration of the gel particles with increasing electrical charge.

(2) (a) The amount of hydrogen ions taken up by gelatin can be calculated with fair accuracy from Langmuir's adsorption equation.

(b) *On this conception, an equation for swelling similar to that of* Wilson and Wilson has been derived.

(3) A *proportionality* between the amount of hydrogen ions adsorbed and the electrical charge has been observed. For hydrochloric, nitric, and trichloroacetic acids the ratio of the electrical charge to the amount of hydrogen ions adsorbed is nearly constant. For sulphuric acid the ratio diminishes with increasing hydrogen-ion concentration.

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XCVIII.—*Researches on Antimony. Part II. Derivatives of Tri-*p*-tolylstibine.*

By ARCHIBALD EDWIN GODDARD and VICTOR EMMANUEL YARSLEY.

FOR the degradation of triarylstibines to diarylhalogenostibines the authors have devised an easier method than those hitherto available, which are either difficult in practice, or applicable only to special compounds (see Hasenbäumer, *Ber.*, 1898, **31**, 2914; Goddard, J., 1922, **123**, 484). The method, which is similar to that by which Morgan and Yarsley (*Proc. Roy. Soc.*, 1926, **110**,

534; see also Morgan and Davies, *Nature*, 1925, **116**, 499) obtained dimethylcyanostibine from trimethylstibine cyanobromide, consists in heating, *e.g.*, tritolylstibine dichloride, dibromide, or di-iodide under diminished pressure; a halogenotoluene distils off, leaving the ditolylhalogenostibine. This work is being continued with the object of degrading diarylchlorostibines to aryldichlorostibines.

Schmidt (*Annalen*, 1922, **429**, 140), by heating triphenylstibine in saturated methyl-alcoholic hydrogen chloride in an atmosphere of carbon dioxide, obtained a small quantity of diphenylstibinic acid and a good yield of diphenylhydroxystibine. The application of this method to tri-*p*-tolylstibine gave a small quantity of the acid, and a little plastic residue which could not be identified as the hydroxide.

A second method used by Schmidt was to treat a hot acetone solution of the triarylstibine with 5*N*-sodium hydroxide and 3% hydrogen peroxide solution, and here the authors agree with him in obtaining a diarylstibinic acid and a diarylstibine trichloride, namely, *ditolylstibinic acid* and *ditolylstibine trichloride*.

Schmidt's methods of degrading diarylhydroxystibines to monoarylstibinous oxides also gave poor results, and the authors used the diazo-reaction in the preparation of *p*-tolylstibinic acid, which was identical with the acid obtained by Hasenbäumer from *p*-tolylstibine tetrachloride by hydrolysis.

Tri-*p*-tolylstibine, on treatment with cold fuming nitric acid, gave *tri*-m-*nitrotri*-p-*tolylstibine dinitrate*. Since tri-*m*-xylylstibine on similar treatment gives tri-5-nitrotri-*m*-xylylstibine dinitrate (Goddard, J., 1923, **123**, 2315), these results together with that of Morgan and Micklethwait (J., 1911, **99**, 2286) seem to show that the nitro-group always enters the nucleus in the meta-position to the antimony.

Hydrolysis of the dinitrate by a large excess of phosphorous acid gave the corresponding *oxide*, whereas Michaelis (*Annalen*, 1902, **321**, 212) showed that trinitrotritolylarsine oxide in presence of phosphorous acid produces the free arsine.

Tri-m-*aminotri*-p-*tolylstibine* was prepared by reducing the nitro-compound with zinc dust and ammonia in alcoholic solution, and converted into *tri*-m-*iodotri*-p-*tolylstibine* by the Sandmeyer reaction.

EXPERIMENTAL.

Di-p-*tolylhalogenostibines*.—Tri-*p*-tolylstibine dichloride (2 g.), when heated under 5—7 mm. pressure, gave *p*-chlorotoluene (b. p. 160°) at 60—65° and *di*-p-*tolylchlorostibine* at 160—200°; after being washed with light petroleum and alcohol, the latter was a white solid (Found: Cl, 10·4. $C_{14}H_{14}ClSb$ requires Cl, 10·45%).

In a similar way, the dibromide (2 g.) gave *p*-bromotoluene (m. p. 23°) at 70—75° and *di*-p-*tolylbromostibine* (obtained, after repeated washing with alcohol, as a pale cream compound, melting above 290° and only slightly soluble in warm organic solvents. Found : Sb, 31·8. $C_{14}H_{14}BrSb$ requires Sb, 31·75%) at 170—210°; and the di-iodide (2 g.) gave *p*-iodotoluene (m. p. 35°) at 80° and *di*-p-*tolyliodostibine* at 180—200°, the latter, after being washed with alcohol and with ether, being a white solid, m. p. 233°, almost insoluble in cold, but soluble in warm, organic solvents (Found : Sb, 28·4. $C_{14}H_{14}ISb$ requires Sb, 28·3%). The yield of di-*p*-tolylhalogenostibine was in each case almost quantitative.

Di-p-*tolylstibinic Acid*, $(C_7H_7)_2SbO{\cdot}OH$.—(1) Tri-*p*-tolylstibine (9 g., suspended in 150 c.c. of methyl alcohol), when mixed with 30 c.c. of methyl alcohol (saturated with hydrogen chloride) and boiled on the water-bath in a current of carbon dioxide, dissolved after 15 minutes. The yellow solution was boiled for 1¼ hours, cooled, and made distinctly alkaline with dilute aqueous sodium hydroxide. The white precipitate produced was removed as a suspension in ether and added to the solid obtained from the aqueous layer by precipitation with acetic acid. Recrystallisation from alcohol gave a white, amorphous product, sintering at 230° and melting at 260°. The yield was very small (Found : Sb, 36·2. $C_{14}H_{15}O_2Sb$ requires Sb, 36·2%).

(2) A solution of 6 g. of tri-*p*-tolylstibine in acetone was gradually added to a boiling mixture of 113 c.c. of water, 37 c.c. of 5*N*-sodium hydroxide, and 22·5 c.c. of 6% hydrogen peroxide. The solution, filtered from a slight precipitate, was treated with dilute sulphuric acid, and the voluminous white precipitate obtained was partly dried, washed with warm alcohol, and recrystallised from benzene (Found : Sb, 35·95%). The acid is slightly soluble in hot or cold alcohol or cold benzene and readily soluble in hot benzene.

Di-p-*tolylstibine Trichloride.*—The precipitate obtained on addition of sulphuric acid as in method (2) was reprecipitated, first from 5*N*-hydrochloric acid as the pyridine double salt and then from dilute sodium hydroxide solution by dilute acetic acid. Thereafter it was dissolved in fairly concentrated, boiling hydrochloric acid, and the solution evaporated to small bulk; the colourless needles of *di*-p-*tolylstibine trichloride* obtained crystallised from benzene in colourless plates, sintering at 130° and melting at 141—142° (Found : Sb, 29·7. $C_{14}H_{14}Cl_3Sb$ requires Sb, 29·7%).

p-*Tolylstibinic Acid*, $C_7H_7{\cdot}SbO_3H_2$.—Two solutions, one of diazotised *p*-toluidine (26 g. of the base, 37 g. of concentrated sulphuric acid, 250 c.c. of water, and 18 g. of sodium nitrite) and the other of 56·6 g. of antimony trichloride in 15 g. of hydrochloric acid

(*d* 1·16) and 41 c.c. of water to which 150 g. of sodium hydroxide in 750 c.c. of water had been added, were mixed at 0° and treated with copper bronze. The liquid was filtered after 2 days, nearly neutralised with dilute sulphuric acid, again filtered if necessary, and acidified with dilute hydrochloric acid. The mixture (50 g.) of *p*-tolylstibinic acid and antimony trioxide obtained was dissolved in 27 g. of hydrochloric acid (*d* 1·16) and 98 c.c. of water, and the boiling solution saturated with solid ammonium chloride. The mixture of *p*-tolylstibinic oxychloride and ammonium chloride that crystallised on cooling was filtered off and dissolved in sodium carbonate solution, and the stibinic acid was precipitated by acidification with dilute hydrochloric acid and crystallised from spirit and from ether. Yield, 8 g. (Found: Sb, 46·3. Calc. for $C_7H_9O_3Sb$: Sb, 46·3%).

Tri-m-*nitrotri*-p-*tolylstibine Dinitrate*, $(C_7H_6{\cdot}NO_2)_3Sb(NO_3)_2$.—Tri-*p*-tolylstibine (5 g.) was slowly added to the calculated quantity of well-cooled fuming nitric acid; and the solution poured into water (1 l.). The *dinitrate*, precipitated as a light cream-coloured powder, after several recrystallisations from alcohol, melted sharply at 182° with frothing. It was soluble in the usual organic media (Found: Sb, 18·9; N, 10·8. $C_{21}H_{18}O_{12}N_5Sb$ requires Sb, 18·6; N, 10·7%).

The position of the nitro-group was determined by heating the compound with bromine and phosphorus pentabromide in a sealed tube at 130° for 4 hours, 4-bromo-2-nitrotoluene, m. p. 45°, being obtained.

Tri-m-*nitrotri*-p-*tolylstibine Oxide*.—The dinitrate (2 g.) was heated for 8 hours with 10 g. of phosphorous acid in 100 c.c. of absolute alcohol, and the solution poured into water (1 l.). The *oxide*, which separated as a cream-coloured powder, was washed with hot water, dried, and crystallised from alcohol, being obtained as a white powder, m. p. 225° after softening at 220°; on further heating, it blackened and became pyrophoric (Found: Sb, 22·0; N, 7·6. $C_{21}H_{18}O_7N_3Sb$ requires Sb, 22·2; N, 7·7%).

Tri-m-*aminotri*-p-*tolylstibine*, $(C_7H_6{\cdot}NH_2)_3Sb$.—The dinitrate (7 g.) was boiled for 8 hours with a solution of 250 c.c. of 90% alcohol containing 5 g. of ammonium chloride, 15 c.c. of aqueous ammonia, and 15 g. of zinc dust, a further 3 g. of zinc dust being added each hour. The solution was filtered at room temperature into water (2 l.). The brown solid obtained was collected and dissolved in 250 c.c. of warm 15% hydrochloric acid, and the filtered solution was treated with concentrated aqueous ammonia until no further precipitate appeared. The crude *amine* was crystallised from chloroform–light petroleum, yielding a pinkish-grey powder, m. p. 92° (Found: Sb, 27·7. $C_{21}H_{24}N_3Sb$ requires Sb, 27·7%).

Tri-m-iodotri-p-tolylstibine.—The amine (3 g.), dissolved in 20 c.c. of concentrated hydrochloric acid and 200 c.c. of water, was diazotised with 2 g. of sodium nitrite, 5 g. of potassium iodide in 50 c.c. of water were added, and the mixture was gently warmed on the water-bath for 3 hours. The precipitate obtained, when crystallised from chloroform–light petroleum, gave a reddish-brown powder, which sintered at 136° and melted at 146° to a dark red liquid (Found: I, 24·4. $C_{21}H_{18}I_3Sb$ requires I, 24·4%).

EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE,
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XCIX.—*Some Properties and Reactions of β-Chloroethyl, β-Cyanoethyl, and β-Carbethoxyethyl Toluene-*p*-sulphonates, including an Extension of the Friedel–Crafts Reaction.*

By GEORGE ROGER CLEMO and ERIC WALTON.

THE introduction of the β-chloroethyl group into phenols has been effected by treating the phenol with β-chloroethyl toluene-*p*-sulphonate, $C_7H_7{\cdot}SO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2Cl$ (subsequently called ester *A*) in the presence of caustic soda, 80% yields of phenyl β-chloroethyl ethers heing obtained (Clemo and Perkin, J., 1922, **121**, 642).

It was thought that the halogen atom in these ethers, on treatment with potassium cyanide, would be replaced to give the β-cyanoethyl ethers, and, on hydrolysis, the β-phenoxypropionic acids. These compounds are troublesome to prepare in quantity by present methods,* and on ring closure give the chromanones, which are valuable for synthetic work on certain natural products. Attempts to effect the replacement of the chlorine atom in the β-chloroethyl ethers by the cyano-group, however, have been unsuccessful.

Attention was then turned to the preparation of β-*cyanoethyl toluene*-p-*sulphonate*, $C_7H_7{\cdot}SO_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, itself, with a view to the direct introduction of the β-cyanoethyl group into phenols. Although this ester can be easily prepared from toluene-*p*-sulphonyl chloride and ethylene cyanohydrin, it has been found to be readily hydrolysed by cold dilute alkalis, and hence it is unsuitable for use as an alkylating agent. When β-cyanoethyl toluene-*p*-sulphonate

* β-Phenoxypropionic acid itself was obtained in a yield of 20% from phenol and β-iodopropionic acid (Bischoff, *Ber.*, 1900, **33**, 924); Arndt and Källner (*Ber.*, 1924, **57**, 202), using β-chloropropionic acid, obtained a 30% yield.

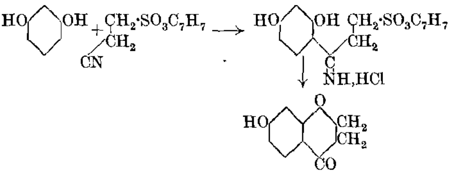
(subsequently called ester B) is treated with anhydrous alcoholic hydrogen chloride, it is easily converted into the *hydrochloride* of *γ-imino-γ-ethoxypropyl toluene-p-sulphonate*, which is hydrolysed by water to give *β-carbethoxyethyl toluene-p-sulphonate*:

$$C_7H_7\cdot SO_2\cdot O\cdot CH_2\cdot CH_2\cdot C(OEt){:}NH,HCl \xrightarrow{H_2O} C_7H_7\cdot SO_2\cdot O\cdot CH_2\cdot CH_2\cdot CO_2Et.$$

This carbethoxy-ester (subsequently termed ester C), although more stable to alkalis than ester B, is, nevertheless, hydrolysed too easily for it to be of use as an alkylating agent for the direct introduction of the β-carbethoxyethyl group into phenols.

(It has been found that various other nitriles, such as β-phenylpropionitrile, react smoothly with cold alcoholic hydrogen chloride, giving good yields of highly crystalline iminoethyl ether hydrochlorides, which are especially useful for the identification of liquid nitriles, and their treatment with water furnishes a very convenient method for the direct conversion of the cyano- into the carbethoxy-group.)

There remained, however, the possibility that the ester B could be applied for the synthesis of the desired chromanones in the well-known Hoesch reaction (*Ber.*, 1915, **48**, 1122) thus:

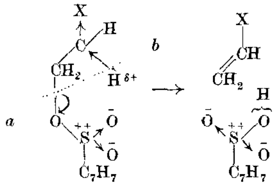


The reaction, however, does not occur in this manner, but the isomeric compound, 7-hydroxy-3 : 4-dihydrocoumarin, is formed in fairly good yield (compare Langley and Adams, *J. Amer. Chem. Soc.*, 1922, **44**, 2320). This constitutes, therefore, a further anomaly of the Hoesch reaction (see Chapman and Stephen, J., 1925, **127**, 885). Neither ester A nor C reacts with resorcinol under similar conditions.

As none of the esters A, B, and C appeared to be suitable for the preparation of the chromanones, attention was directed to a comparison of their reactions. Ester A was relatively very stable to alkalis, being hydrolysed to the extent of only 25% after boiling for 2 hours with 2 equivalents of 2*N*-sodium hydroxide; on being shaken with the same proportion of alkali at the ordinary temperature, ester B was hydrolysed completely in 4 minutes to acrylo-

nitrile and toluene-p-sulphonic acid, and ester C in 40 minutes to acrylic ester and the sulphonic acid. This ease of hydrolysis was also well shown when ester B was warmed at 80° with anhydrous potassium carbonate, acrylonitrile distilling in 75% yield. This method for preparing acrylonitrile is therefore much superior to those described by Moureu (*Bull. Soc. chim.*, 1893, **9**, 424; 1920, **27**, 903: yields, 30% and 47% respectively). In a similar manner, when the ester C was heated with anhydrous potassium carbonate at about 100°, a quantitative yield of ethyl acrylate was given off. The same behaviour was shown when the three esters A, B, and C were treated with potassium phthalimide. In the first case phthal-β-chloroethylimide was produced, and with B and C, acrylonitrile and acrylic ester, respectively, distilled.

The marked difference in the ease of the alkaline hydrolysis of the esters A, B, and C can be explained in the following manner:



When X represents either the cyano- or the carbethoxy-group, both of which commonly act as electron-sinks, electron displacements occur which produce slight intramolecular ionisation, with the result that the hydrogen atoms of the CH_2X group acquire a small positive charge. Further, as two of the oxygen atoms of the sulphonic group are joined to the sulphur atom by semi-polar double bonds, *i.e.*, have, according to Lowry, a negative charge, there is an urge for the molecule to split, as shown, along *ab*. In ester A, however, the chlorine atom is not an electron-sink, but behaves much as it does in alkyl chlorides, so that the hydrogen atoms do not become positively charged, and hence the molecule is relatively stable. This explanation, rather than one involving a co-ordinated hydrogen atom, would appear to be borne out by the boiling points of the esters, which rise in the order A, C, B; whereas if it be supposed that the split along *ab* is facilitated by a co-ordinate link between one of the oxygen atoms and a hydrogen atom, then the expected order of ascending boiling points would be, according to Sidgwick's work, B, C, A.

The fact that, in the alkaline hydrolysis of the esters B and C,

the cyano- and the carbethoxy-group remained intact caused attention to be directed to the action of the Grignard reagent on these esters. Gilman and Beaber (*J. Amer. Chem. Soc.*, 1923, **45**, 839; 1925, **47**, 518) have described the action of organic magnesium halides on alkyl sulphonates, and in particular that of magnesium phenyl bromide on the ester A, in which case β-chloroethylbenzene resulted. When esters B and C are substituted for A in this reaction, violent action occurs and no definite compounds have been isolated from the resulting complex mixtures.

In contrast with this result, however, it has now been found that when the ester A is treated with benzene in the presence of aluminium chloride a good yield of dibenzyl results, whereas, under similar conditions, the esters B and C undergo reaction very smoothly at the sulphonic ester linking alone, with the direct production of good yields of β-phenylpropionitrile and ethyl β-phenylpropionate respectively:

$$2C_6H_6 + C_7H_7{\cdot}SO_3CH_2{\cdot}CH_2Cl \xrightarrow{AlCl_3} C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$$

$$C_6H_6 + C_7H_7{\cdot}SO_3CH_2{\cdot}CH_2{\cdot}CN \text{ (or } CO_2Et) \xrightarrow{AlCl_3} C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CN \text{ (or } CO_2Et).$$

This modification of the Friedel–Crafts reaction along apparently new lines furnishes a very convenient method for the production of alkylated aromatic hydrocarbons, and the action, which is being further investigated, appears capable of considerable extension, as a great variety of sulphonic esters of the type A are obtainable. For instance, in the simple case, from ethyl toluene-*p*-sulphonate, benzene, and aluminium chloride, a 65% yield (approximately) of ethylbenzene, calculated on the ester used, has been obtained.

EXPERIMENTAL.

β-*Cyanoethyl Toluene*-p-*sulphonate* (ester B).—This compound is readily prepared by boiling a mixture of pure toluene-*p*-sulphonyl chloride (190 g.), ethylene cyanohydrin (100 g.), and xylene (150 c.c.) under reflux for about 3½ hours. Hydrogen chloride is rapidly evolved at first, and later the mixture darkens with the separation of *ammonium toluene*-p-*sulphonate* (25 g.) in colourless prisms, m. p. 325—330° (Found: N, 7·4; S, 17·0. $C_7H_{11}O_3NS$ requires N, 7·4; S, 16·9%). The mixture is steam-distilled to expel the xylene, and the residue poured into cold water (2000 c.c.). Ester B, which separates as an oil and quickly solidifies, is dried on a porous plate and recrystallised from methyl alcohol (yield, 146 g. or 65%) (Found: C, 53·0; H, 5·2; N, 5·8; S, 14·5. $C_{10}H_{11}O_3NS$ requires C, 53·3; H, 4·9; N, 6·2; S, 14·2%). It crystallises from benzene

and alcohol in colourless prisms, and from water, in which it is only slightly soluble, in needles, the melting point of both varieties being 64°; it boils at 187—189°/0·5 mm. without decomposition.

γ-Imino-γ-ethoxypropyl Toluene-p-*sulphonate Hydrochloride.*—A mixture of ester B (10 g.) and a saturated solution of hydrogen chloride in absolute alcohol (50 c.c.) is shaken at room temperature until all the solid has dissolved, and then, after 1—1½ hours, slowly diluted with anhydrous ether (200 c.c.). The *hydrochloride* of the iminoethoxypropyl ester, which crystallises, is washed with dry ether until free from hydrogen chloride, and recrystallised from absolute alcohol, containing a trace of hydrogen chloride, by slow addition of dry ether (yield, about 11 g. or 81%) (Found: S, 10·4; Cl, 12·1. $C_{12}H_{17}O_4NS,HCl$ requires S, 10·4; Cl, 11·5%). It crystallises in colourless leaflets, m. p. 101°, is fairly stable in air, but dissolves easily in, and is readily hydrolysed by, water.

β-Carbethoxyethyl Toluene-p-*sulphonate* (ester C).—This ester quickly separates as an oil when a solution of the above imino-salt (10 g.) from ester B in water (50 c.c.) is warmed to 70°. It is isolated by means of ether, dried, and fractionated, the portion distilling at 167—169°/0·2 mm. being collected (yield, 7·5 g. or about 85%) (Found: C, 52·8; H, 5·9; S, 11·7. $C_{12}H_{16}O_5S$ requires C, 52·9; H, 5·9; S, 11·8%). The ester C is a colourless syrup, insoluble in water. It distils with slight decomposition into acrylic ester and the sulphonic acid, even in a very good vacuum, and is readily hydrolysed into the same two compounds by cold aqueous alkalis.

7-Hydroxy-3 : 4-dihydrocoumarin.—A mixture of ester B (9 g.), resorcinol (6·1 g.), and zinc chloride (1 g.) in anhydrous ether (80 c.c.) is saturated with dry hydrogen chloride. The crystals obtained after 4 hours, when washed free from traces of oil and acid with ether and dissolved in water (50 c.c.), decompose with separation of the dihydrocoumarin as an oil, which soon solidifies to a crystalline compound (m. p. 133°), similar in all respects to that obtained by Langley and Adams (*loc. cit.*) from β-chloro-propionitrile and resorcinol. The yield is 3·2 g. (49%) (Found: C, 66·1; H, 5·2. Calc.: C, 65·8; H, 4·9%).

Acrylonitrile.—An intimate mixture of ester B (9 g.) and anhydrous potassium carbonate (4·5 g.) is heated carefully with occasional stirring. At about 80° acrylonitrile begins to distil, and at 120°, when some water follows, the heating is stopped, and the distillate dried over calcium chloride and fractionated; the greater portion passes over at 77—79° (yield, 1·6 g. or 75%) (Found: C, 68·1; H, 6·0; N, 26·9. Calc.: C, 67·9; H, 5·7; N, 26·4%).

Ethyl Acrylate.—Similarly this ester may be prepared by carefully heating a mixture of ester C (10·8 g.) and anhydrous potassium carbonate (4 g.). It passes over at a little above 100°, is dried over calcium chloride and fractionated, almost the whole distilling at 100—101°; the yield (3·9 g.) is approximately theoretical (Found: C, 59·3; H, 7·8. Calc.: C, 60·0; H, 8·0%).

Phthal-β-chloroethylimide.—A mixture of potassium phthalimide (9·5 g.) and ester A (11·7 g.) is heated for about 3 hours at 200° with occasional stirring. The cooled mass is extracted with boiling water, and the residual oil, which solidifies, is crystallised two or three times from alcohol; it then melts at 79—81° (compare Seitz, *Ber.*, 1891, **24**, 2626). The yield of crude product is 9 g. or 86% (Found: Cl, 17·4. Calc.: Cl, 17·0%).

Dibenzyl.—A mixture of ester A (11·7 g.), benzene (100 c.c.), and aluminium chloride (20 g.) is heated under reflux for 2 hours, and the product, when cool, is poured into dilute hydrochloric acid (600 c.c.) and steam-distilled; 7 g. of dibenzyl (b. p. 284°; m. p. 51°) are obtained from the distillate by fractionation.

β-*Phenylpropionitrile.*—When ester B (11·2 g.) is submitted to the treatment described in the preceding paragraph (benzene, 80 c.c.; aluminium chloride, 10 g.), β-phenylpropionitrile is obtained as an oil, b. p. 254° (yield, 4·7 g. or 72%) (Found: C, 82·3; H, 6·9. Calc.: C, 82·5; H, 6·9%).

Ethyl β-*Phenylpropionate.*—This also is obtained in a similar manner from ester C (13·6 g.), benzene (80 c.c.), and aluminium chloride (10 g.) (yield, 6·6 g. or 74%); b. p. 245° (Found: C, 74·3; H, 7·8. Calc.: C, 74·2; H, 7·9%).

Ethylbenzene.—Ethyl toluene-*p*-sulphonate (30 g.) is dissolved in benzene (150 c.c.), and aluminium chloride (30 g.) added. After the evolution of hydrogen chloride, which is at first spontaneous, has somewhat abated, the mixture is refluxed for 2 hours and then worked up as in the above cases. The portion of the distillate passing over at 133—137° (10·2 g. or 64%), on refractionation, distils almost wholly at 135°, the b. p. of ethylbenzene (Found: C, 90·6; H, 9·35. Calc.: C, 90·6; H, 9·4%).

γ-*Imino*-γ-*ethoxy*-α-*phenylpropane Hydrochloride.*—β-Phenylpropionitrile (2·5 g.) is dissolved in a concentrated ethyl-alcoholic solution of hydrogen chloride (15 c.c.). The solution, which becomes warm, is kept for about 2 hours and is then slowly diluted with anhydrous ether (150 c.c.). The *hydrochloride* of the corresponding iminoethoxy-compound, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl$, which crystallises, is recrystallised from a solution in absolute alcohol, containing a trace of hydrogen chloride, by the gradual addition of ether, and then forms needles, m. p. 130° (yield, 3·1 g. or about

76%) (Found : Cl, 16·6. $C_{11}H_{15}ON,HCl$ requires Cl, 16·6%). It dissolves very readily in water, quickly hydrolysing to ethyl β-phenylpropionate (yield, more than 95%).

α-Chloro-γ-imino-γ-ethoxypropane Hydrochloride.—To a solution of acrylonitrile (1 g.) in dry ethyl-alcoholic hydrogen chloride (15 c.c.), which has been kept for about 2 hours, anhydrous ether (150 c.c.) is slowly added; the *hydrochloride*, $CH_2Cl·CH_2·C(OEt):NH,HCl$, formed by the addition of a further molecule of hydrogen chloride to the carbon–carbon double bond, then crystallises. The compound can be recrystallised as described above for the iminoethoxy-salt from β-phenylpropionitrile (yield, 2·1 g. or about 65%) [Found : Cl (total), 41·8; Cl (ionic), 20·4. $C_5H_{10}ONCl,HCl$ requires Cl (total), 41·3; Cl (ionic), 20·6%]. It forms colourless plates, m. p. 109°, and dissolves very readily in water with hydrolysis into ethyl β-chloropropionate.

One of us (E. W.) wishes to thank the Trustees of the Westmorland Society (London) for an exhibition enabling him to take part in this investigation; and also the Chemical Society for a grant which has partly defrayed the cost of research materials.

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NEWCASTLE-UPON-TYNE. [*Received, January 26th*, 1928.]

C.—*Properties of Conjugated Compounds. Part IV. The Formation of Isomeric Additive Dibromides from Butadiene.*

By ERNEST HAROLD FARMER, CYRIL DUNN LAWRENCE, and JOCELYN FIELD THORPE.

CERTAIN conjugated hydrocarbons have been found to yield additive dibromides and hydrobromides of two types, representing attachment of the addendum at adjacent and at terminal carbon atoms of the chain, respectively. This fact would seem to constitute direct evidence in favour of that attractive extension of the Thiele hypothesis which has been developed in connexion with electronic theories of polarisation. It is held that the butadienoid unit may polarise in two ways, $C—C—\overset{+}{C}—\overset{-}{C}$ and $\overset{+}{C}—C—C—\overset{-}{C}$, leading to reaction at adjacent (1 : 2- or 3 : 4-) or terminal carbon atoms of the chain. On this basis terminal addition is no longer *required*, but may be explained when it arises during the course of experiment. With precisely those conjugated compounds, however, from which

two isomeric additive products have been isolated, there is evidence to show that one additive form is readily convertible into the other. The question therefore arises whether both are primary products of addition.

The addition of bromine to butadiene was examined by Griner (*Compt. rend.*, 1893, **116**, 723; **117**, 553). This author records the formation (in chloroform solution at $-21°$) of only one dibromide. This substance, a liquid, changed slowly in the cold and rapidly at 100° into a solid isomeride, m. p. 53—54°. The liquid and the solid were respectively considered to be the 1 : 2- and the *trans*-1 : 4-dibromide of butadiene. Conversion of the liquid form into the solid, by heating, was not complete : a small amount of liquid dibromide remained which, although almost undifferentiated in boiling point from the original liquid form, was considered to be the *cis*-1 : 4-dibromide. The accuracy of these observations was contested by Thiele (*Annalen*, 1899, **308**, 333), who stated that under essentially the conditions of Griner the predominant product of bromine addition was the solid, m. p. 53—54°. The constitution of a small liquid residue was left undetermined. Since the 1 : 4-position of the bromine atoms in the solid compound followed readily from its oxidation product, butadiene was regarded as yielding mainly—probably exclusively—a terminal dibromide. Although the additive formation of both 1 : 4- and 1 : 2-dibromides has more recently been admitted by Thiele (Straus, *Ber.*, 1909, **42**, 2872), there is, as far as we are aware, no record in the literature of a repetition of the experiment.

Under the conditions described by both Griner and Thiele, butadiene invariably unites additively with bromine to yield a mixture of two dibromides. One of these, a liquid which corresponds to Griner's product in boiling point and instability, is the 1 : 2-dibromide, since its ozonide on fission gives excellent yields of αβ-dibromopropaldehyde and formaldehyde; the other is the solid compound described by Griner and Thiele and shown by the latter to possess the 1 : 4-constitution.

$$CH_2Br{\cdot}CHBr{\cdot}\overset{\frown O_3 \frown}{CH{-}CH_2} \longrightarrow$$
$$H{\cdot}CHO + CH_2Br{\cdot}CHBr{\cdot}CHO \; (\xrightarrow{-HBr} CH_2{:}CBr{\cdot}CHO)$$

When *either* the 1 : 2- or the 1 : 4-dibromide is heated for a few minutes at 100°, the product is a mixture in which the two isomerides appear to be in equilibrium [1:2 ⟶ 1:2 (20%) + 1:4 (80%) ⟵ 1:4]. The 1 : 2-constitution of the liquid portion of the mixture, whether derived by the forward or by the backward change, has been established by ozonisation. *No indication of the formation of a third*

isomeride (the *cis*-1 : 4-dibromide of Griner) has been obtained; * if, however, the heating be prolonged for several hours, a new liquid of considerably higher boiling point, probably a polymeride, makes its appearance. At room temperature the change 1 : 2- $\longrightarrow$ 1 : 4- takes place slowly and approaches completion in about four days if crystallisation of the solid form be promoted; if crystallisation is not assisted, the system tends apparently to a metastable condition. *At room temperature the reverse change is inappreciable.* Both dibromides readily liberate iodine from potassium iodide dissolved in acetic acid. The liberation is most rapid with the 1 : 2-dibromide, but quantitative measurements are rendered difficult owing to the recombination of the liberated iodine with the bromohydrocarbon. Figures approaching one molecule of liberated iodine per molecule of dibromide have been obtained.

In a series of theoretical papers (*Bull. Soc. chim. Belg.*, 1921—1922) Gillet has reviewed many known cases of intramolecular change among unsaturated compounds. These involve migration of an atom or radical (OH, Br, H) with accompanying double-bond movement. *He submits the generalisation*: "*If in the system* $C_1{:}C_2{\cdot}C_3X$ the total effect of the radicals saturating C_3 is strongly negative in comparison with that of the groups saturating C_1, the most negative radical attached to C_3 tends to migrate to C_1" (*ibid.*, 1922, **31**, 365). The additive dibromides and dihydrogenated derivatives of conjugated compounds would be expected to exemplify this rule, and of the former Gillet says: "If one compares the compound $CH_2{:}CH{\cdot}CHBr{\cdot}CH_2Br$ with the examples cited (examples which follow the rule) it is found to be in the same category and should very easily undergo, under the influence of traces of acid, the transformation $CH_2{:}CH{\cdot}CHBr{\cdot}CH_2Br \longrightarrow CH_2Br{\cdot}CH{:}CH{\cdot}CH_2Br$. *Thus in effect two forms are obtained by combining one molecule of bromine with one molecule of butadiene, the second form preponderating.*" Addition is therefore regarded as taking place at one double bond, the apparent 1 : 4-addition being sufficiently explained by including the 1 : 2-dibromide in the category of substances subject to "negative" migration.

During *the course of our experiments* Prévost has published observations (*Compt. rend.*, 1927, **184**, 1460) concerning the addition of bromine to $\alpha\alpha\delta\delta$-tetramethylbutadiene. Here the dibromide

* Owing to the mobility of the liquid dibromide and the ready solubility of the solid dibromide in its liquid isomeride (also the volatility of the former in the vapour of the latter) it is particularly difficult to demonstrate conclusively, as, *e.g.*, by oxidation or distillation methods, the absence of a *cis*-1 : 4-isomeride. This point is being closely examined in the less mobile bromo-compounds derived from certain substituted butadienes.

consists of a mixture of solid (10—20%) and liquid material when first isolated, but the liquid portion solidifies so rapidly, and decomposes so readily on distillation, that a definite liquid dibromide isomeric with the solid compound cannot be separated. The solid is regarded as the 1 : 4-form, and the liquid as a solution of this form in its 1 : 2-isomeride. From indications afforded by the variation of the melting point of the solid form with rapidity of heating and of the rapidity of solidification of the fused mass with duration of heating, it is concluded that the behaviour of the isomerides conforms with a principle of tautomeric interchange similar to that laid down by Gillet, but reversible. The re-statement of Lapworth's $\alpha\gamma$-rule on a basis of ionisation ("synionism") by this author (*ibid.*, 1927, **185**, 132) is of interest in that it identifies the activated form of the system A:B·CX with the ionised form $A\pm B\mp C\pm,X\mp$, employing the nomenclature of alternate polarity. The inclusion of additive dibromides of butadienoid hydrocarbons among mobile propene systems has, however, only an indirect bearing on the additive mode of the conjugated hydrocarbons unless (1) the primary additive dibromide is invariably a 1 : 2-compound, or (2) the tautomeric complex, $CH_2Br \cdot \dot{C}H \cdot CH{:}CH_2$, is in some form a necessary feature of the additive mechanism. If the sole primary additive dibromide of butadiene is the 1 : 2-compound, then the proportion of the two isomerides in the crude bromination mixture might be expected to vary with those conditions which affect the 1 : 2- → 1 : 4-change. Actually, although the proportion of isomerides obtained during bromination shows great constancy under given experimental conditions, it varies widely with the solvent employed. The table shows the percentage of 1 : 4-dibromide obtained in the presence of four carefully purified solvents, pure bromine being employed.

Chloroform	(−15°), 63·0.	Acetic acid	(4°), 70·0.
Hexane	(−15°), 38·4.	Carbon disulphide	(−15°), 65·9.

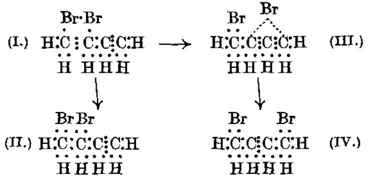
The rate at which the pure 1 : 2-dibromide isomerises in solvents such as hexane and chloroform, at temperatures below 20°, is variable but very slow. Change which occurs subsequently to the formation of the 1 : 2-dibromide and in which only the latter compound and the solvent participate, appears, therefore, an insufficient explanation of the considerable percentages of 1 : 4-dibromide recorded. The employment of slightly impure (commercial) instead of pure solvents during the bromination process caused little variation from the figures given above. Hydrogen bromide suggests itself as a probable accelerator of the 1 : 2- ⟶ 1 : 4-change, particularly as it is produced (apparently inevitably) during the bromin-

ation of butadiene. This reagent does undoubtedly accelerate the change in solution, but the extent of acceleration (see p. 738) falls far short of that which would be required for the formation of 38—70% of 1 : 4-dibromide during the time occupied by, and at the temperature of, bromination. Attempts to decrease the concentration of hydrogen bromide during bromination by suspending or dissolving appropriate reagents in the solvent led only to comparatively small reductions in the proportions of 1 : 4-dibromide (p. 737).

Although in a newly formed, extremely mobile system, the product isolated could be other than that first formed, in the present instance the degree of mobility appears insufficient to account for a considerable degree of 1 : 2 ⟶ 1 : 4-change within the required limits of time and temperature, unless acceleration is to be attributed to energy changes associated with a progressing reaction. It appears from this result that isomeric change of a purely post-additive nature is not to be regarded as mainly responsible for the appearance of two kinds of additive product. It remains, therefore, either to attribute the constitutional differentiation of the products to an inherent capacity of the hydrocarbon for assuming differently polarised forms, or to regard it as in large measure incidental to the operation of the additive mechanism. Of these alternatives, only the latter needs consideration, one of the principal objects of the present series of investigations being to examine the possibility of accounting for the additive products of so-called conjugated compounds without having recourse to a special hypothesis of conjugation.

It is clear that if reversible $\alpha\gamma$-change of the type ·CBr·C:C ⇌ C:C·CBr (considered as purely of an intimate intramolecular character—that is to say, not proceeding by effective ionisation of bromine) is comparatively slow when the substances in question are the formed molecules of 1 : 2- and 1 : 4-dibromide, it is necessary to look to an earlier stage in the additive process for the chief cause of the differential orientation of the additive products. Thus, there is every appearance of the possession by an *intermediately* formed molecule or additive complex of a mobility superior to that of the corresponding formed molecules (compare " the enhanced mobility of *newly formed* molecules," Ingold and Goss, J., 1925, **127**, 2776). If, then, the additive reactions of butadienes are fundamentally of normal ethylenic character, the first additive stage of butadiene should be identical with that of ethylene under analogous conditions. Since in non-ionising solvents at any rate, there is strong probability of molecular attack by bromine (compare Soper and Smith, J., 1926, 1582; 1927, 2757) the intermediate compound may be represented (electronically) by a formula such as (I), although,

possibly, attachment of the addendum at the two carbon atoms is achieved successively rather than simultaneously.



This has only transient existence, and breaking of the singlet linkage between the bromine atoms allows activity in two ways: (*a*) taking the course normal in the bromination of ethylenes, yielding (II), (*b*) bringing into action the tautomeric capacity of the propene system and passing through (III) to (IV). In this way conditions tending to the initiation of the $\alpha\gamma$-change (an absence of that fixity appertaining to the formed molecules which restrains the progress of the 1:2- $\rightleftharpoons$ 1:4-change) occur in the normal course of addition, and activity of the propene system, in the sense indicated, is rendered the more probable by knowledge of propenoid behaviour derived from other sources. There is, of course, nothing in the evidence now submitted which definitely excludes the possibility of the formation of two intermediate complexes (corresponding to alternative polarisations of the hydrocarbon) in the additive process, but the observations recorded indicate a method of diminishing the probability in this direction by demonstrating the adequacy of propenoid activity to account for the differentiation of additive products.

Experiments with the additive dibromides of other butadienoid hydrocarbons have shown that reversible interconversion of 1 : 2- and 1 : 4-forms takes place either spontaneously or on heating (unless heating causes degradation). Little is known as yet concerning the equilibration of these compounds in solution or the correspondence (in composition) of equilibrium mixtures obtained under different conditions. Therefore, it is not possible to gauge the degree of approach to a condition of equilibrium between 1 : 2- and 1 : 4-forms attained in the bromination process. Doubtless, however, modification of the butadiene system by the introduction of substituents will have an effect on the composition of original bromination products generally analogous to that of substituents in aromatic processes and approximating towards that exerted in the 1 : 2- $\longrightarrow$ 1 : 4-change in the sense foreseen by Gillet. Experiments

in this direction are now being made, employing variously substituted butadienes and addenda of different types.

EXPERIMENTAL.

$\Delta^{\alpha\gamma}$-Butadiene was readily obtained from the gas which is liberated on heating "railway hydrocarbon"; this was passed into bromine until decolorisation was complete. The product became semi-solid on cooling owing to separation of butadiene tetrabromide. The latter compound was filtered off, washed with ligroin, and twice recrystallised from the same solvent (m. p. 117°; compare Thiele, *loc. cit.*). The filtrate contained a quantity of the stereoisomeric tetrabromide (m. p. 37—39°), but since this was difficult to purify in comparison with the higher-melting compound, the former was used exclusively for regenerating butadiene. The method of Thiele (*loc. cit.*) was employed for regeneration, the tetrabromide being placed in a percolator, from which condensed alcohol from the reaction flask gradually removed it. The issuing gas, after passing through efficient water-cooled condensers, was scrubbed by passage through U-tubes packed with calcium chloride and maintained at 0°. The gas was directly absorbed by solvent maintained at a low temperature, the quantity absorbed being estimated from the increase in weight. Owing to the ease with which butadiene is lost from many solvents, a content figure considerably lower than that indicated by weighing was assumed in the following bromination experiments. The yield, when the gas was absorbed in chloroform, was usually about 80%.

Method of Bromination.—A solution of the hydrocarbon in the desired solvent was prepared in a flask closed by a stopper carrying the delivery tube and a calcium chloride tube. After the weight of dissolved hydrocarbon had been ascertained, the stopper was rapidly exchanged for one carrying a small dropping-funnel and a calcium chloride tube. The required quantity of bromine was introduced into the dropping-funnel, which was then closed by a calcium chloride tube. The flask was cooled in a freezing mixture of ice and salt and the contents thereof were kept in thorough agitation during the entire period of bromination (about 1 hour for 5 g. of hydrocarbon). On opening the flask, fumes of hydrogen bromide usually escaped. The solvent, except in the case of acetic acid, was evaporated at greatly reduced pressure without heat-application. In those experiments in which glacial acetic acid was employed the bromination mixture was divided into two equal portions, which were worked up in different ways, and the results were compared. From one portion the solvent was removed at greatly reduced pressure, the containing flask being immersed in a

beaker of water at 25°, whereas from the other it was removed by pouring the mixture into water, extracting the dibromide with ether, and repeatedly washing the ethereal solution with water. The subsequent removal of ether from the dried solution was conducted at reduced pressure. The total yield of dibromide and the proportion of solid dibromide were found to be nearly identical for each method.

Purification of the reagents was effected as follows : Bromine : (1) method of West, J., 1924, **125**, 1279; (2) a process essentially the method 3 of Orton, Watson, and Hughes (J., 1927, 2462). Acetic acid : method of Backes, West, and Whiteley (J., 1921, **119**, 364). Chloroform : washing with water, followed by agitation with concentrated sulphuric acid and final distillation over phosphoric oxide. Carbon disulphide : shaking with metallic mercury, followed by distillation over phosphoric oxide. Hexane : sodium-dried *n*-hexane of commerce (b. p. 68—69°) first carefully fractionated under an efficient column, then refluxed for 6 hours over sodium wire, and finally distilled. Quinoline dibromide hydrobromide was recrystallised twice from alcohol [Found : Br, 64·2 (total); 42·5 (available). Calc. : Br, 64·8 (total); 43·2 (available)%].

Separation of Dibromides.—The mixture of dibromides was diluted with an equal volume of petroleum (b. p. 40—60°) and cooled gradually (to obtain compact crystals) to −20°. After remaining at this temperature for 1 hour, the mother-liquor was decanted from the crystals, which were rapidly washed by decantation with a further very small amount of petroleum, the washings being added to the mother-liquor. The process was twice repeated. The liquid dibromide was isolated from the ultimate mother-liquor by evaporation of the solvent at reduced pressure. In the earlier experiments the halogen content of the crude liquid was determined; in each case so determined, the value found corresponded very closely with the required figure and the estimation was subsequently dispensed with. Owing to slight loss by volatilisation during the removal of the solvent, the total yield of dibromide in each experiment was slightly in deficit (usually about 1½%) of the theoretical quantity calculated on the basis of the bromine employed.

The solid dibromide, αβ-dibromo-Δ^{β}-butene, crystallised in colourless prisms, m. p. 53° (Found : Br, 74·8. Calc. : Br, 74·8%). The intensely lachrymatory nature of this substance rendered it very objectionable to work with. The liquid dibromide was a colourless, mobile oil, which distilled without degradation (b. p. 58—66°/14 mm.), but suffered in the process a considerable degree of conversion into its solid isomeride (Found : Br, 74·7%).

Constitution of the Liquid Dibromide.—A solution of purified dibromide (6·5 g.) in chloroform was cooled in a freezing mixture

vhilst submitted to a current of ozonised oxygen (8 hours). The olvent was removed at reduced pressure, and the colourless, viscous ozonide decomposed by warming it gently with water. The formal-lehyde, which was fully evolved during the decomposition, was absorbed in dilute ammonia and subsequently recovered as iexamethylenetetramine. The aqueous liquor, which contained nuch oil in suspension, was extracted with ether, the extract being haken with a little sodium bicarbonate solution and finally dried. Distillation of the solvent (the distillate containing formaldehyde) eft a pale yellow aldehydic oil, rich in bromine. This substance, αβ-dibromopropaldehyde, was converted for convenience into α-bromoacraldehyde by heating on a steam-bath for 20 minutes vith aqueous sodium acetate (10 g. in 10 c.c.). The resulting iquor yielded on steam distillation a pale yellow, lachrymatory oil, b. p. 55°/17 mm. (Found: C, 26·7; H, 2·0; Br, 59·4. Calc.: C, 26·7; H, 2·25; Br, 59·25%), which was strongly aldehydic, yielding a semicarbazone, m. p. 160°, identical with that of α-bromoacral-lehyde prepared by the method of Auwers and Heyna (*Annalen*, 1923, **434**, 140). The yields were excellent.

Composition of the Bromination Mixture.—The percentages of the 1:4-dibromide obtained in the different experiments are hown in the table. The figures are calculated on the ratio of 1:4-dibromide to the total dibromide isolated; the figures in brackets are the corresponding values based on the amount of bromine employed. The solvents and brominating agent were carefully purified, except where indicated as ordinary commercial reagents (com.).

Solvent.	Brominating agent.	Added reagent.	1:4-Dibromide %.
Chloroform.	Bromine.	—	63·0 (62·5)
,,	Quinoline dibromide hydrobromide.	—	0
Chloroform (*com.*).	*Bromine* (*com.*).	—	63·7 (62·1)
Hexane.	Bromine.	—	38·4 (36·5)
,,	,,	Quicklime.	36·3 (35·2)
,,	,,	Calcium carbonate.	36·9
Acetic acid.	,,	Potassium acetate.	69·2 (66·3)
Acetic acid (*com.*).	Bromine (*com.*).	—	70·3 (67·6)
Carbon disulphide.	Bromine.	—	65·9 (64·0)

Interconversion of the Butadiene Dibromides.—The liquid dibromide isomerises slowly even at room temperature. The change became appreciable in 3—4 days as indicated by diluting a specimen vith petroleum and cooling to −15°; the introduction at this stage of a large crystal of the solid dibromide usually led to almost complete conversion into the solid isomeride in the course of a few days, but specimens left undisturbed remained liquid after standing for several weeks. At higher temperatures isomerisation was more rapid and

at 100° conversion to the extent of about 80% could be effected in a few minutes. The solid form, stable at room temperature, likewise suffered isomerisation at higher temperatures. The identity of the liquid bromide so produced with the 1 : 2-dibromide derived directly from butadiene followed from its boiling point, its re-convertibility into the 1 : 4-dibromide, and the formation of formaldehyde and α-bromoacraldehyde on decomposition of its ozonide: there was no indication of a third isomeride, the *cis*-1 : 4-dibromobutene of Griner. The effect of heating the 1 : 4-dibromide at 100° over periods varying from 10 minutes to 3 hours was in all cases to produce a mixture of 1 : 2- and 1 : 4-isomerides. There was every appearance that at 100° equilibrium between the two forms became very rapidly established, since the composition of the mixtures produced by heating for periods up to ¾ hour varied little (solid 80%, liquid 20%); gradually, however, owing to slight degradation and the accumulation of a by-product of high boiling point (probably polymeric), the composition became changed and after 3 hours only 68% of the mixture consisted of the solid isomeride.

A knowledge of the facility of isomerisation of the liquid dibromide when dissolved in solvents such as chloroform and maintained under temperature conditions similar to those employed during bromination was a matter of importance. Specimens of the pure liquid dibromide, dissolved in hexane or chloroform at —15° and maintained for appropriate periods at this temperature, were found on examination (by the method utilised in separating the products of bromination) to have suffered only slight change, amounting to not more than a few units %. The change under similar conditions with acetic acid was rather greater but still small. The introduction of small quantities of hydrogen bromide into solutions of the pure liquid dibromide appeared to have in every case a definite accelerating effect, but this was not marked, amounting, for example, with chloroform only to 8% conversion. In no instance was a considerable conversion in solution effected at a low temperature and even at room temperature the degree of conversion became important only after a prolonged period.

Lability of Bromine in Butadiene Dibromides.—Both 1 : 2- and 1 : 4-dibromides liberated iodine from a glacial acetic acid solution of potassium iodide at room temperature. With the former the initial speed of liberation was the greater, but after a time the progress of the reaction could not be followed owing to the combination of iodine with the unsaturated compounds in solution. At 40° the combination of liberated iodine was still more marked. No really satisfactory method of estimation was discovered, although by periodic titration of the reaction mixture with concentrated thio-

sulphate solution (carrying out simultaneously a control experiment) a liberation of nearly 0·9 mol. of iodine per mol. of dibromide was registered in each case. The time taken was about 7 hours.

It is desired to express our thanks to Dr. A. T. Healey for gifts of crude hydrocarbon, and to the Government Grant Committee of the Royal Society for a grant which has defrayed a portion of the cost of this research.

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CI.—*Selenium Oxyfluoride.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and CHARLES BERESFORD COX.

BY the action of fluorine on selenium, Moissan (" Le Fluor," p. 123) obtained white fumes and a white solid, which were not further examined. If the fluorine contained electrolytic oxygen (as is often the case) or was mixed with air, it is possible that the fumes contained an oxyfluoride, and the residue would then have consisted of selenium dioxide, or selenious acid containing a little hydrofluoric acid. Lebeau (*Compt. rend.*, 1907, **145**, 190) reported a gaseous fluoride of selenium which he considered to be the hexafluoride previously discovered by one of us (J., 1906, **89**, 316), but since this contained about 2% of selenium in excess of the theoretical proportion, the presence of an oxyfluoride was suspected. In our opinion this is improbable because the gas had been kept in a gas-holder over mercury, which would have decomposed an oxyfluoride. Lebeau also stated that separation of oxyfluoride from hexafluoride by fractional distillation would have been difficult, but we now know that there is a sufficient difference between the boiling points, for the hexafluoride sublimes at $-39°$.

No definite oxyfluoride of selenium had therefore been described until our preliminary experiments (J., 1927, 928) showed that it was probably produced by the interaction of selenium oxychloride and silver fluoride. These results are now confirmed and amplified.

EXPERIMENTAL.

Conditions of the Reaction.—The selenium oxychloride, supplied by the British Drug Houses, did not require redistillation. The silver fluoride was prepared by the method of Ruff (" Das Fluor "), or by evaporating a solution of the acid fluoride and drying the product in a heated desiccator; the latter material was reactive,

but still contained a little acid, probably as silver hydrogen fluoride, since the acid came over first in the subsequent distillation.

When the vapour of selenium oxychloride was passed over heated silver fluoride contained in a platinum boat, the fluoride was quickly converted into chloride, a white sublimate of selenium dioxide was observed, and the glass was strongly etched. Reaction occurred in dry carbon tetrachloride with similar results. Experiments were then carried out in a platinum bottle with platinum condenser tube, but little if any gas was produced. When the bottle was heated to about 140° on a sand-bath, the reaction suddenly began with the production of copious fumes; these condensed in the platinum tube to a colourless liquid, the analysis of which proved that it was selenium oxyfluoride, $SeOF_2$. The yield was low because some vapour escaped owing to the rapidity of the reaction, and some remained in the bottle at the end of the distillation. Even with excess of silver fluoride, the reaction was sometimes incomplete because the grains of fluoride were coated with silver chloride, as proved by the fact that, although the aqueous extract of the residue contained no soluble silver, some was found in the filtrate obtained when the residue was dissolved in ammonia and reprecipitated with nitric acid.

Preparation.—Selenium oxychloride (9—10 g.) and about 3 times its weight of silver fluoride were thoroughly mixed with a platinum stirrer, and heated until the commencement of the violent reaction, which was moderated as required by cooling the bottle. Alternatively, the silver fluoride was added in two or three portions to the oxychloride, the mixture being well stirred and heating being continued until a portion showed no ionic chlorine after reaction with water. The whole was then distilled between 140° and 200° and the distillate was collected in a platinum crucible with a tight lid; the analyses of successive portions have already been given (*loc. cit.*), and the properties were constant. After removal of the residue from the platinum bottle, this was used for storage, being tightly closed and kept in a desiccator with calcium chloride.

In later experiments, the compounds were mixed in a large platinum crucible which was contained in a monel-metal pot of 1¾ inches internal diameter. (This was made to our specification by Mr. E. R. Walter, B.Sc., to whose skill we are also indebted for the other pieces of apparatus made of monel metal.) The screw cover of the pot was provided with an inlet tube through which a current of dry air was passed at the end of the distillation. The products of several experiments were then collected in the platinum bottle and a sufficient quantity was thus obtained for the determination of the melting point.

Analysis.—The previous methods of analysing mixtures of hydrofluoric and selenious acids (J., 1926, 167) have now been further improved and tested on mixtures of known composition. The procedure is briefly as follows: The solution of the two acids was titrated with $N/10$-alkali (free from carbonate) to the end-point shown by *p*-nitrophenol, which falls somewhat short of the point corresponding to sodium fluoride and sodium hydrogen selenite.

[The factor for this correction of the observed titre (V c.c.) was 1·03 in the particular mixture under investigation, *i.e.*, $2HF + H_2SeO_3$.] Rather more than $2/3V$ c.c. of $N/10$-silver nitrate were added, and the precipitation of silver selenite was completed by the addition of further alkali until the yellow colour of the indicator reappeared. The precipitate was then collected in a waxed funnel, and the titration completed on the filtrate and washings in the presence of phenolphthalein. The total alkali used gave correctly the sum of the acids. The silver selenite, preferably precipitated from a separate portion, was washed, finally with alcohol, and dried at 110—120°. The selenium so found agreed with that determined as element.

A mixture corresponding to $SeO_2 + 2HF$ was made by distilling 4 mols. of the anhydrous acid on to a weighed quantity of the dioxide and adding the necessary additional amount of dioxide. The analyses of the mixture and of the compound followed the same course. The sample was weighed quickly in a platinum crucible with a tightly fitting lid; this was then immersed in water contained in a large platinum basin, and rolled about so as to admit the water so slowly that no fumes escaped at any stage. As an example of the results obtained, we quote the analysis of a sample taken from the preparation which was used in the determination of the melting point: 0·9132 g. was dissolved to give 97·88 g. of solution in a ceresined flask; 44·25 g. of this solution gave 0·2440 g. of selenium (as element) and hence the selenium content of the sample was 59·1%. 12·23 G. of the solution required altogether 40·0 c.c. of $N/10$-alkali (*i.e.*, before and after precipitation of silver selenite); of this, the selenious acid required 19·8 c.c., as calculated from a gravimetric determination, and therefore the hydrofluoric acid required 20·2 c.c., corresponding to 28·9% of fluorine in the sample (Calc. for $SeOF_2$: Se, 59·5; F, 28·5%).

Physical Properties.—On account of the corrosive action of this compound, especially upon glass, it has only been possible to determine the density, the boiling point, and the melting point. The preparations used in these determinations all gave satisfactory analyses by the above methods.

Density. A thick-walled tube, made by drilling out a rod of monel metal, was fitted with two lids which could be screwed down against a flange inside and also against a lead washer, which was held between the lid and the top of the tube. Two similar tubes of this pattern were used, one as a density bottle, the other as a boiling-point and reaction bottle. The lid of the density bottle was centrally bored with a hole 1/32 inch in diameter and was prolonged into a plunger below the screw thread. The bottle was calibrated with water in the usual way. Its capacity was about 0·5 c.c. Found: $d = 2{\cdot}70, 2{\cdot}64, 2{\cdot}66$; mean 2·67.

Boiling point. This was determined by the method of Smith and Menzies (*Z. physikal. Chem.*, 1911, **75**, 494). The monel-metal bottle was closed by a lid carrying a piece of tubing of ⅛ inch internal diameter, which was bent through 180°. The end (below the bottom of the boiling-point bottle) was drilled to 3/16 inch diameter. Into this end was fitted a short length of platinum tube, the other end of which was sealed into a capillary glass tube, in which could be observed the fluctuations of the vapour pressure. The bottle was about three-quarters filled with the selenium oxyfluoride, attached to a thermometer, and heated in a bath of bromonaphthalene or medicinal petroleum. The temperature at which a steady stream of bubbles first appeared was about 100°, but this did not correspond to the true boiling point, since the temperature of the bath rose much higher, and liquid was still found on opening the bottle. A number of readings were made of the temperature at which the liquid sucked back; this point was determined about a dozen times as 121—129°, with 5 readings at 124°.

Melting point. In anticipation of a low value, a pentane thermometer was used, which had also been found accurate at the ordinary temperature. In the first two determinations, which gave rather higher values than that stated below, the bulb of the thermometer was protected by a thin glass tube coated with sulphur. The lag, however, was too great to allow of trustworthy readings, especially with the small quantity of liquid then available The bulb was therefore sheathed in platinum foil, wound tightly round, and pressed together at the bottom. The liquid was poured into the smallest platinum vessel, which was placed in the bottom of a thinly vaselined glass tube, tightly closed by a rubber bung bearing th thermometer and a drying tube. The liquid was solidified, not to quickly, by immersion of the outer tube in a mixture of alcohol an carbon dioxide snow, being thus obtained as a clear, dark mass, lik ice. This was allowed to melt slowly by placing the tube inside vacuum cylinder. A heating curve was taken from the time wh liquid was first observed; in the presence of solid and liquid, t

emperature fluctuated irregularly between 4·5° and 4·7° for 10 ninutes, and then rose slowly; hence melting point = 4·6°.

Chemical Reactions.—Glass is rapidly attacked by the liquid or rapour with the formation of a white deposit, consisting principally of selenium dioxide. Silica, as a dry powder, reacts violently with the liquid. An attempt to analyse the compound by means of this reaction showed that the evolution of silicon tetrafluoride is nearly quantitative: $2SeOF_2 + SiO_2 = 2SeO_2 + SiF_4$.

Crystalline silicon is slightly attacked in the cold, readily on warming. The fine powder was added to some of the compound in the boiling-point bottle, which was connected with a nitrometer containing dry mercury. On heating, gas was evolved, some of which was absorbed by water and shown to be silicon tetrafluoride. The residual silicon was coated with red selenium, and also contained selenium dioxide; the amounts of these were 0·078 and 0·166 g., respectively, the theoretical amounts from the 0·400 g. of selenium oxyfluoride taken being 0·119 and 0·167 g. respectively, in accordance with the equation $Si + 2SeOF_2 = SiF_4 + SeO_2 + Se$.

Red phosphorus, which had been extracted with alkali and thoroughly dried, ignited in a few seconds when mixed with the compound. The oxyfluoride was placed in the monel bottle, the bent tube of which was filled with the phosphorus, and connected with a nitrometer containing dry mercury. When the bottle was warmed, the vapour reacted very suddenly, filling the nitrometer with gas and with red fumes of selenium and phosphorus. The gas was very quickly absorbed by dilute alkali, and the resulting solution, after filtration, was shown to contain combined phosphorus; the gas was therefore probably phosphoryl fluoride and not phosphorus trifluoride, for the latter is very slowly absorbed by alkali and not by water. The reaction probably occurs mainly according to the first of the equations given below.

Sulphur (octahedral) as a powder is not attacked in the cold, but on warming, a gas is evolved, and red selenium is deposited.

Alcohol mixes readily with the compound, as it does with both the dioxide and hydrogen fluoride. Carbon tetrachloride forms two layers.

The Solution $SeO_2 + 2HF$.

It has already been shown that under ordinary conditions selenium dioxide does not combine with hydrogen fluoride with the elimination of water (J., 1926, 168). Solutions of the dioxide in hydrogen fluoride resemble in many respects the compound described above, and it was therefore deemed of interest to determine the constants and behaviour of the mixture in the above ratio. The preparation and analysis of this mixture have been described above.

The reaction with phosphorus was even more violent than in the case of the oxyfluoride, and seemed to increase with the concentration of the selenium dioxide, for the mixture $SeO_2 + 4HF$ showed scarcely any action until the excess of acid had evaporated. The reaction was investigated quantitatively in the boiling-point bottle. The gas was first treated with water, which slowly absorbed 4·9 c.c. (POF_3), and then with alkali, which slowly absorbed 6·6 c.c. (PF_3). The reaction therefore probably takes place in two ways:

$$6(SeO_2 + 2HF) + 4P = 4POF_3 + 5Se + H_2SeO_3 + 5H_2O$$

$$6(SeO_2 + 2HF) + 4P = 4PF_3 + 3Se + 3H_2SeO_3 + 3H_2O.$$

Silicon was attacked with steady evolution of gas. Sulphur was hardly affected in the cold, but on heating, a deposit of red selenium was formed, sometimes with inflammation. Monel metal was slightly attacked after a time, with the production of a red solution which probably contained colloidal selenium.

Changes in Volume during Solution and Hydrolysis.—The determination of the densities of this solution and of the compound (see table) furnishes an unusually favourable set of data for the comparison of changes of volume which occur during the course of a complete dissolution and a complete hydrolysis yielding the same product, under isothermal and isobaric conditions. Halides of the non-metals, other than fluorides, on hydrolysis yield gases which can only be kept in the system under high pressures, *e.g.*, phosphorus oxychloride gives off hydrogen chloride, and the mode of combination of the elements in the products of hydrolysis is extremely doubtful. Fluorides of many non-metals are themselves gaseous and cannot be compared under isobaric conditions with the products of hydrolysis. In the present case, however, solids and liquids react to form a solution which almost certainly should be written as $SeO_2 + 2HF$, since it is extremely improbable that hydrogen is removed from direct combination with fluorine. The partial formation of a complex, such as hydrofluoselenious acid, $H_2SeO_2F_2$, is not likely to involve a considerable change of volume. We can compare the volume changes of reactions (1) and (2) by using the densitie given in the table, together with those of selenium dioxide (3·954 and hydrogen fluoride (0·988).

$$SeO_2 + H_2F_2 \longrightarrow (SeO_2 + 2HF) \quad . \quad . \quad . \quad (1)$$

Molecular volumes $27{\cdot}55 + 40{\cdot}50\ (= 68{\cdot}05) \longrightarrow 58{\cdot}5$

$$SeOF_2 + H_2O \longrightarrow (SeO_2 + 2HF) \quad . \quad . \quad . \quad (2)$$

Molecular volumes $49{\cdot}2 + 18{\cdot}0\ (= 67{\cdot}2) \longrightarrow 58{\cdot}5$

Both of these reactions proceed with considerable evolution of he from left to right. The contractions, 9·55 and 8·70, are ve

similar, and if the volume of the SeO, which is common to all the systems, is constant, then the molar volume of H_2O is scarcely altered when its elements are divided between SeO and F_2.

Comparison of Properties.

	$SeOF_2$.	$SeO_2 + 2HF$
Density.	2·67	$2{\cdot}57_5$
Molar volume.	49·2	58·5
Melting point.	+ 4·6°	*Indefinite.*
Boiling point.	+124·0°	Indefinite.
Effect of distillation.	Constant distillate; no residue.	Distillate contains much HF and little SeO_2. Residue of SeO_2.
Se content (by analysis).	59·5% (58·0—59·9)	52·4%
Action on sulphur.	Not perceptible in the cold; evolution of gas and deposition of red Se on heating.	Similar.
Action on silicon.	Slight in cold; evolution of SiF_4, deposition of Se on heating.	Steady evolution of SiF_4.
Action on red phosphorus.	Violent, with inflammation; evolution of gaseous fluorides of phosphorus; production of red Se and of SeO_2.	Similar.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, February 1st*, 1928.]

CII.—*The Action of Bromine Water on Certain Olefinic Acids.*

By JOHN READ and WILLIAM GALLOWAY REID.

IN the course of investigations upon the use of chlorine water and bromine water as effective sources of hypochlorous and hypobromous acids, it has been shown that these reagents react readily with cinnamic, methylcoumaric, and methylcoumarinic acids to form halogenohydrins. In ice-cooled aqueous solutions, at concentrations varying from 0·07*N* to 0·08*N*, and under appropriate conditions, from 95% to 98% of the reacting unsaturated acid was transformed to the chloro- or bromo-hydrin, the remainder giving rise to the corresponding dihalogenide (Read and Andrews, J., 1921, **119**, 1774). Similar results have been recorded for other unsaturated acids by Biilmann (*Rec. trav. chim.*, 1917, **36**, 317), who found that bromine water reacted with fumaric and maleic acids in 0·05*N*-aqueous solutions, forming bromohydrin to the extent of about 96%. Corresponding values for the remaining acids investigated by Biilmann were as follows: *crotonic acid* (0·05*N*), 100%;

acrylic acid (0·1*N*), 98%; mesaconic acid (0·05*N*), 75%; and itaconic acid (0·1*N*), 68·5%.

During a study of the application of chlorine and bromine water to various types of unsaturated organic substances, we have examined the effect of concentration upon the interaction between bromine water and some of the above olefinic acids and their sodium salts. With maleic acid, 89·3% of the reacting bromine was converted into bromohydrin and hydrobromic acid in a 0·05*N*-aqueous solution, under the conditions adopted; the proportion fell to 81·9% in a 0·10*N*-solution and to 62·5% in a 0·33*N*-solution. Maleic acid thus behaves very similarly to ethylene and allyl alcohol, which appear to be the only unsaturated substances hitherto examined over a range of concentrations in this manner (Read and Hook, J., 1920, **117**, 1214; Read and Hurst, J., 1922, **121**, 989). Sodium maleate, in aqueous solutions of equivalent concentrations, decolorised bromine water with several hundred times the rapidity of free maleic acid; at the same time, the proportions of bromohydrin were distinctly enhanced, and the graph connecting these proportions with the corresponding concentrations became practically rectilinear over the range of concentrations examined. These results are summarised in the appended table:

Percentages of Total Bromine reacting to form Bromohydrin and Hydrobromic Acid.

Maleic acid.		Sodium maleate.		Sodium fumarate.		Itaconic acid.	
N.	%.	*N*.	%.	*N*.	%.	*N*.	%.
0·0500	89·3	0·0500	95·6	—	—	0·0482	96·6
0·0655	87·5	0·0655	95·0	0·0666	96·9	0·0642	96·0
0·1000	81·9	0·1000	92·5	0·1000	95·0	0·0962	94·9
0·1667	74·3	0·1667	87·5	0·2000	89·3	0·1923	89·8
0·3334	62·5	0·3334	75·6	—	—	0·2748	86·3

Interaction between fumaric acid and bromine water was exceec ingly slow in the experiments undertaken; sodium fumarate, hov ever, brought about decolorisation with approximately half tl speed of sodium maleate, and furnished proportions of brom hydrin slightly higher than those afforded by the latter salt (con pare Lossen, *Annalen*, 1906, **348**, 261). Free itaconic acid ga closely similar results, the conversion into bromohydrin being mu more complete than in Biilmann's experiments. Coumarin und went bromination in the benzene nucleus when treated with bromi water, thus resembling methylcoumaric and methylcoumarinic ac (Read and Andrews, *loc. cit.*).

Oleic acid reacted also with bromine water, but in this insta only 51·5% of the bromine was effective in forming bromohyd ... temperature, in an approximately decinor

mixture containing some potassium bromide. It was formerly considered essential to conduct the addition of hypochlorous and hypobromous acids to unsaturated compounds in the absence of bright light and at a low temperature; but it has been demonstrated that direct sunlight exerts no apparent influence in the formation of halogenohydrins, according to the methods described, from cinnamic, methylcoumaric, and methylcoumarinic acids (*loc. cit.*), and in the case of ethylene it promotes the reaction (J., 1920, **117**, 1221). An interesting result illustrating the effect of heat was observed in the reaction between indene and bromine water, which appears to be practically unaffected by raising the temperature from 2° to 90° (Read and Hurst, J., 1922, **121**, 2550); we now show, further, that with oleic acid the yield of bromohydrin obtained from fixed weights of the reactants is actually increased when the aqueous emulsion is raised from the ordinary temperature to about 90°. When treated in succession with alcoholic potassium hydroxide and dilute sulphuric acid, the crude product from this last reaction gave a dihydroxystearic acid, m. p. 92—93°. Albitzky (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 76) prepared two stereoisomeric dihydroxystearic acids from the chlorohydrin obtained from either oleic acid or elaidic acid: these melted at 93—95° and 127—128°, respectively. We were unable to attain the melting point, 99—100°, recorded by Saytzeff (*ibid.*, 1892, **24**, 477) and also by Albitzky (*loc. cit.*) for specimens of a dihydroxystearic acid prepared by somewhat different methods.

EXPERIMENTAL.

Maleic Acid.—1. An aqueous solution of maleic acid (10 g. in 250 c.c.) was slowly added at the ordinary temperature to water (500 c.c.) into which a current of air charged with bromine vapour was introduced through a perforated glass bulb (J., 1920, **117**, 359). The liquid was stirred continuously, and the conditions were adjusted so as to maintain an excess of maleic acid in a distinctly yellow solution until no more bromine appeared to be absorbed (16 hours). Unchanged bromine was then removed by passing air through the liquid. The hydrobromic acid formed in the reaction, which was determined titrimetrically, corresponded to the conversion of 26·4% of the maleic acid into bromohydrin; the results given below indicate, however, that the solution contained some unchanged maleic acid. A crystalline deposit of dibromosuccinic acid (2 g., m. p. 255°) separated during the reaction, and a further quantity of this substance was obtained upon concentrating the filtrate.

2. In a further series of experiments, maleic acid was dissolved

in water, together with a molecular proportion of bromine, to form solutions of known concentrations. The mixtures were kept in stoppered flasks at the ordinary temperature in diffused daylight until the bromine was completely absorbed; the amounts of hydrobromic acid produced were then determined in the usual way. The proportions of bromine functioning to form bromohydrin and hydrobromic acid at various concentrations are given in the table on p. 746. Dibromosuccinic acid separated from the solution only in the first of these experiments. In all instances the bulk of the bromine was absorbed within the first 2 days, but complete decolorisation of the solutions took about a week.

Sodium Maleate.—Series (2) above was repeated with the modification that in each case the maleic acid was exactly neutralised with sodium hydroxide before the bromine was added. The bromine was absorbed rapidly, decolorisation being effected within 30 minutes.

Sodium Fumarate.—The interaction between fumaric acid and bromine water was so slow, even under the conditions adopted with success for cinnamic acid (J., 1921, **119**, 1776), that attention was restricted to examining the effect of the reagent on sodium fumarate. The results of a series of experiments, conducted as described in the preceding paragraph, are in the table. Complete absorption of the bromine occupied from 1 to 2 hours.

Itaconic Acid.—When mixed with a molecular proportion of bromine in aqueous solution, itaconic acid reacted much more rapidly than maleic acid, complete decolorisation occurring within an hour under the conditions adopted.

Coumarin.—A solution of coumarin (10 g.) in hot 2*N*-sodium hydroxide (100 c.c.) was diluted with water (750 c.c.) and added drop by drop to ice-water (900 c.c.) containing a little sulphuric acid (2 g.); bromine vapour was simultaneously admitted into the liquid in the usual way, with continuous stirring, for a period of about 5 hours. The viscid syrup obtained by extracting the product with ether gradually deposited small colourless needles when kept; after recrystallisation from alcohol, this substance melted at 159—160°, and was found to be identical with 5-bromocoumarin prepared from 5-bromosalicylaldehyde by Perkin's reaction (compare *Ber.*, 1900, **33**, 2327) (Found: Br, 35·75. Calc. for $C_9H_5O_2Br$: Br, 35·55%). The main product yielded by the coumarin consisted of a viscid liquid with the irritating odour characteristic of halogenohydrins, but no further definite substance was isolated from it. Owing to the occurrence of nuclear substitution, with the formation of hydrobromic acid, the distribution of the bromine could not be ascertained.

Oleic Acid.—To 10 g. of oleic acid, emulsified in 250 c.c. of water at the ordinary temperature, was gradually added a molecular proportion of bromine (5·67 g.) dissolved in aqueous potassium bromide (10 g. in 75 c.c.). The mixture was shaken vigorously throughout the addition. The whole of the bromine was absorbed, and a determination of the resulting hydrobromic acid showed that 51·5% of the halogen had reacted to form this substance and bromohydrin. When the operation was repeated at about 90°, this proportion rose to 57·5%. The ethereal extract yielded in each instance a thick, brown oil, which did not crystallise.

A portion (7·5 g.) of the product from the second experiment was boiled for 2 hours with alcoholic potassium hydroxide (2·5 g. in 90 c.c.); the bulk of the solvent was distilled off, and the residue was heated for an hour on the water-bath with an excess of dilute sulphuric acid. The ethereal extract furnished a syrup from which glistening leaflets (1·2 g., m. p. 92—93°) gradually separated; these appeared to consist of a dihydroxystearic acid (Found: C, 68·0; H, 11·1. $C_{18}H_{36}O_4$ requires C, 68·35; H, 11·4%).

Related investigations are in progress.

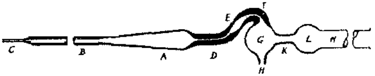
UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, February 6th*, 1928.]

NOTES.

A New Pipette. By H. NORMAN RIDYARD.

THIS pipette combines the essential principle of that of Jakowkin (*Z. physikal. Chem.*, 1899, **29**, 626) with some features of the pyknometer, and was designed for the accurate delivery of small volumes of bromine–benzene solutions.

FIG. 1.



A gently tapering bulb, *A*, is joined at the lower end to a stem of capillary tubing (1—1½ mm.), *B*, which is drawn out at the lower end to a jet, *C*, of very fine bore. The upper end of *A* merges into a very fine capillary, *D*, which bends and expands, as shown, into the small bulb *E*, contracts into the capillary *F*, slightly wider than *D*, and finally enters the bulb *G* (2 cm. diam.). The portion from the junction with *B* to the end of *H* is drawn in one piece

from glass tubing wider than *A*, as joins impede draining. The external diameter of *D*, *E*, *F*, should be over 8 mm. to reduce risk of breakage. The optimum sizes of the capillaries at *C* and *D* vary with the viscosity of the liquid to be used. The upper portion of the pipette may be a straight tube, or of the form *K*, *L*, *M*, which can be packed with glass wool and soda-lime, etc.

The pipette is filled by suction, facilitated by a piece of rubber tubing, *H* being closed by a finger. When *G* is half full, thus receiving all liquid which may have changed in concentration, the pipette is turned with *H* downward, liquid in *G* blown out, and the level of liquid adjusted to the middle of *D* by applying filter-paper to *C*. The contents may then be blown out.

Two pipettes (1·7 c.c., 2·3 c.c.) were examined by weighing seven deliveries. Errors did not exceed $\pm$ 0·02% with water, or $\pm$ 0·1% with benzene. The pipettes delivered 0·1—0·2% more benzene than water under similar conditions.

The author's thanks are due to Professor A. J. Allmand for his guidance and continual encouragement during the work in the course of which this pipette was developed.—UNIVERSITY OF LONDON, KING'S COLLEGE. [*Received, January 20th*, 1928.]

A Reaction of Caryophyllene. By DAVID T. GIBSON.

THE fact that Deussen (*J. pr. Chem.*, 1927, **117**, 282) has just published the results of an investigation on the extension of Buchner's reaction (*Ber.*, 1913, **46**, 2680) to caryophyllene makes it desirabl to describe a reaction of that sesquiterpene which was discovere in the course of a similar study, and was to have been included i a subsequent publication.

When a solution of diazoacetic ester in caryophyllene (b. p 124°/12 mm., $n_D^{18°}$ 1·5012) is gradually added to an excess of caryo phyllene at 180—200° in presence of finely divided copper, a *cycl* propane ester (compare Deussen, *loc. cit.*), b. p. 130—160°/2 mm can easily be separated from the excess of the hydrocarbon. Th ester is not derived from a casual impurity, for the recover caryophyllene continues to give as good a yield on repeated trea ment. The ester is hydrolysed by 10% alcoholic potash, t alcohol and any uncombined oil are distilled in steam, and t potassium salt decomposed with acid. The crude *cyclopropa* acid may readily be crystallised from ligroin, benzene, or acetic aci it has m. p. 165°, and $[\alpha]_{5461}$ − 40° in alcohol (c = 1) (Found : 77·4; H, 9·7; equiv., 248; *M*, in camphor, 268. $C_{16}H_{25}$·CO requires C, 77·8; H, 10·0%; *M*, 262). The acid is stable to brom

in chloroform, and is only very slowly attacked by boiling acid permanganate. The mother-liquor from its crystallisation contains a resinous acid, which is the sole product when more concentrated alkali is used in the hydrolysis.

This test was applied to the fraction of supa oil which Henderson, M'Nab, and Robertson (J., 1926, 3077) had shown to consist largely of copæne. Ethyl diazoacetate (20 g.) in supa oil (120 c.c.) was added drop by drop to supa oil (80 c.c.) at 165° in presence of copper. 165 C.c. of supa oil were recovered unchanged, and after the usual treatment, 1·5 g. of the pure *cyclo*propane *acid isolated*; m. p. 165°, unaltered by admixture with a specimen prepared from caryophyllene. The presence of caryophyllene in that sample of supa oil was confirmed, though much less readily, by the preparation from it of Wallach's caryophyllene alcohol, m. p. 94°. No analogous acid was obtained from either cadinene or cedrene.—THE UNIVERSITY, GLASGOW. [*Received, February 4th*, 1928.]

CIII.—*The Burning of Carbon Disulphide. Part II. The Velocity of the Uniform Movement of Flame in Carbon Disulphide–Second Combustible–Air Mixtures.*

By ALBERT GREVILLE WHITE.

IN previous communications (J., 1922, **121**, 2561; 1927, 793) the author has shown that near the limits for the propagation of flame the burning of carbon disulphide is markedly hindered by the presence of any one of a large number of other combustibles, and has suggested that the limit combustion of carbon disulphide is catalysed, probably by some product of its combustion. The abnormal behaviour exhibited by the disulphide is now shown to extend throughout the whole range of inflammable carbon disulphide–air mixtures.

The experimental method employed was to determine the velocity of the uniform movement of flame that often occurs when a quiescent inflammable gas–air mixture is ignited at the open end of a long, horizontal, uniform, cylindrical tube closed at the other end. This glass tube was 2·5 cm. in internal diameter and generally 3·9 m. long, but for certain determinations shorter tubes were used. The purification of the materials and the method of making up the gas mixtures have been described in former communications. The mixtures were made up in separate vessels, and always contained approximately 1·0% of water vapour. The firing tube was filled

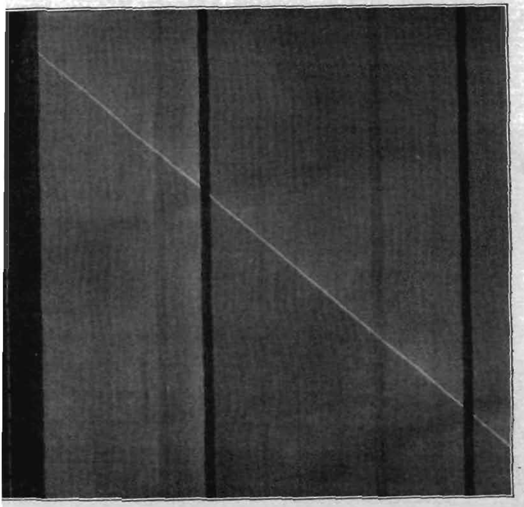
by displacement, the amount of gas used being always at least 6 times the volume of the tube. Ignition was by means of a gas flame of standard size at a flanged joint from which a cap was gently removed immediately before ignition. The actual flame-speed determination was carried out by a novel photographic method which will be fully described in connexion with the work for which it was evolved. In this the firing tube was traversed by an approximately parallel beam of light falling on a photographic plate or film moving at a known speed. The interception of light by the moving flame was shown on the photographic record by a line of which the inclination to the vertical gave a measure of the speed of the flame. A falling-plate camera made by the Cambridge Instrument Co. was used for most of the work. A powerful source of light was essential for the more actinic flames, particularly those containing about 8% of carbon disulphide in air : a 500-c. p. Pointolite lamp was found to be quite suitable. The type of record obtained is shown in Fig. 1.

For most of the mixtures examined duplicate experiments gave results agreeing to about 1%. Mixtures containing from 7 to 12% of the disulphide in air, however, occasionally gave flame speeds 20% or even more below the values normally obtained, whilst high values were also encountered on rare occasions. For these mixtures the results given are not the mean of all those obtained, but the values around which most of the results appeared to be grouped. One record indicated that the speed of an 8% mixture of carbon disulphide in air had changed while being photographed, and suddenly dropped to about 80% of its original value. An occasional mixture exhibited no real uniformity of flame movement at all, although, so far as was known, no change had been made in the experimental conditions. Instances of this were infrequent, but when they occurred it could often be observed that the flame was subdividing, so that one portion remained behind or even went backwards on occasion. All percentage figures given refer to % by vol.

Carbon Disulphide–Air Mixtures.

The speeds of flame normally given by carbon disulphide-air mixtures are shown in Table I and, for mixtures containing up to 20% of the disulphide, in Fig. 2. The maximum speed of flame observed was greater than that given by hydrocarbons of the paraffin series, but considerably below that given by acetylene or hydrogen. The maximum flame speed is given by a mixture containing approximately 8% of carbon disulphide, whereas the mixture for perfect combustion contains nearly 6·5%. In its general form the curve shown in Fig. 2 is similar to that given by another endothermic compound, *viz.*, acetylene. It was not con-

Fig. 1.

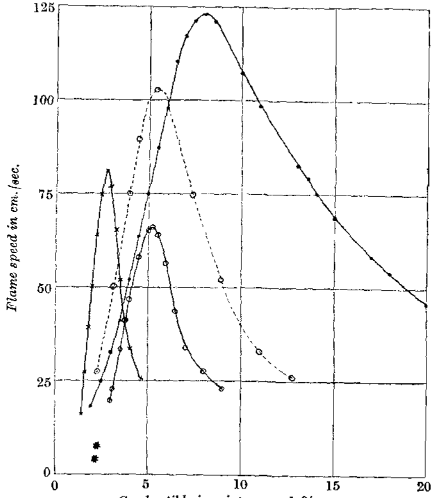


Photographic record for 4·5% CS_2 in air.

[*To face p.* 752.]

tinued to the upper limit owing to the fact that a mixture saturated with the disulphide at the laboratory temperature still propagated flame.

Fig. 2.



Flame speeds for various gas–air mixtures.

* *and* —●—●—●— *Carbon disulphide.*
—×—×—×—×— *Light petroleum.*
⊖-⊖-⊖-⊖ $3CS_2$ + 1 *light petroleum (determined)*
- - o - - - o - - $3CS_2$ + 1 *light petroleum (calculated).*

Whilst examining mixtures near the lower limit it was discovered that certain mixtures could propagate flame with either one or other of two widely differing speeds. It has been shown by Bone (*Proc. Roy. Soc.*, 1927, *A*, **114**, 402) that one gas mixture may give speeds of uniform movement of flame differing by as much as 50% in consecutive experiments, and somewhat similar results have been obtained in this work by using carbon disulphide mixtures of fastest speed of flame. In those experiments, however, no means was found of controlling the speed to be given by any mixture. In the experi-

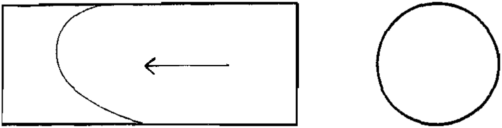
TABLE I.

Speed of uniform movement of flame in carbon disulphide–air mixtures in 2·5 cm. tubes. Original temperature of mixture 17° ± 4°.

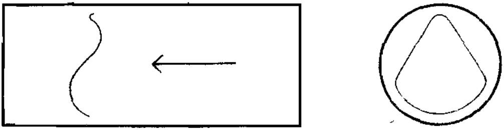
% CS_2 in mixture.	Flame speed (cm./sec.).	% CS_2 in mixture.	Flame speed (cm./sec.).	% CS_2 in mixture.	Flame speed (cm./sec.).
2·00	18·1	5·50	87·0	14·0	74·9
2·10	19·2	6·00	97·8	15·0	68·6
2·15	20·0	6·50	110	17·0	58·1
2·20	21·0 (4·0)	7·00	117	18·0	54·0
2·30	21·8 (7·4)	7·50	121	20·0	45·6
2·50	24·8	8·00	123	25·0	34·5
3·00	32·4	8·50	121	26·0	32·7
3·50	40·6	10·0	107	30·0	27·2
4·00	52·1	11·0	98·2	35·0	23·5
4·50	63·5	13·0	82·4	40·0	21·6
5·00	74·9	13·5	79·1		

The figures in brackets show the speed of a different type of combustion in the same mixture.

FIG. 3.



Normal flame.



Slow (cool) flame.

The two flame types shown by certain carbon disulphide–air mixtures.

ments now being considered, the speed always corresponded fairly closely to one of two values, and the flame could be made to travel with the higher or lower speed at will by varying the means of ignition. Given powerful ignition, the speed of flame was that shown by the full curve in Fig. 2, but with weak ignition the values shown by asterisks were obtained. For a 2·20% mixture one of the speeds is more than 5 times the value of the other. The two flames differed considerably in appearance, as indicated in Fig. 3. The phenomenon could only be observed with a very limited range of

mixtures, for with a disulphide content below 2·20% the low-speed flame could not propagate, whilst from 2·35% upwards it appeared to be unstable, changing more or less rapidly into the form giving a higher speed, and at the same time increasing in velocity. The low-velocity flame only occupied a part of the cross-section of the tube, and only burnt a relatively small quantity of the gas mixture. These observations indicate that the passage of a flame through a gas may not be the invariable process it is sometimes assumed to be, and add another to the list of examples of gas mixtures in which the value of the limit obtained depends upon the type of ignition utilised. Another curious observation was made with a mixture containing approximately 43% of the disulphide—in this case the flame travelled along the top of the tube towards the closed end and then returned to the open end as a slower flame filling the whole tube.

Carbon Disulphide–Second Combustible–Air Mixtures.

The effect of other combustibles on the burning of carbon disulphide was originally tested by determining the speed of flame in a mixture containing 4·5% of carbon disulphide in air of which a portion was progressively replaced by various combustibles. The speeds of flame obtained in these circumstances are shown in Table II and in Fig. 4. These at once show that the abnormal burning of the disulphide is not confined to mixtures near the limit, since for the four combustibles tested the speed curves fall below that for added disulphide, whilst for three out of the four a portion of the curve falls below the speed of the original disulphide mixture.

TABLE II.

Showing the effect of replacing some of the air in a mixture containing 4·5% of carbon disulphide in air by various other combustibles. All mixtures contain sufficient oxygen for complete combustion to CO_2, SO_2, and water.

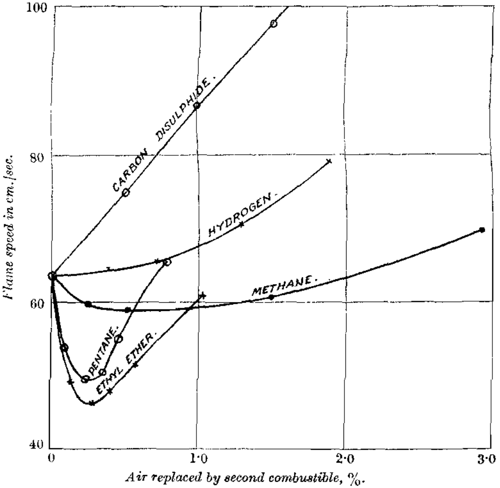
Original temperature of mixtures 17° ± 3°.

Combustible substituted for air.	Flame speed (cm./sec.).	Combustible substituted for air.	Flame speed (cm./sec.).
None	63·5	None	63·5
0·25% of methane	59·7	0·39% of hydrogen	64·4
0·50% ,, ,,	58·9	0·71% ,, ,,	65·4
1·50% ,, ,,	60·6	1·29% ,, ,,	70·5
2·93% ,, ,,	69·6	1·90% ,, ,,	79·2
0·084% of n-pentane	53·7	0·135% of ethyl ether	49·1
0·23% ,, ,,	49·6	0·27% ,, ,,	46·3
0·37% ,, ,,	50·4	0·40% ,, ,,	47·9
0·455% ,, ,,	55·1	0·67% ,, ,,	51·4
0·78% ,, ,,	65·5	1·03% ,, ,,	60·8

The results in Fig. 4 do not enable us to make a sound comparison of the effect of various other combustibles on the burning of the disulphide, for they are affected both by the intrinsic speed value of the added combustible and by its oxygen requirements. The first of these factors is generally the more important. Its effect can be eliminated by mixing carbon disulphide–air mixtures with those of air and a second combustible having the same

Fig. 4.

Showing the effect of replacing some of the air in a 4·5% mixture of carbon disulphide in air by other combustibles.



speed of flame, both mixtures having either an excess or a deficit of oxygen. The results of some of the experiments carried out on these lines are in Table III, together with the results obtained by mixing gas or vapour–air mixtures containing just sufficient oxygen for perfect combustion.

The results of the first series are shown graphically in Figs. 5 and 6. These indicate that for mixtures containing carbon disulphide and air : (1) complex mixtures have lower flame speeds than mixtures

TABLE III.

Showing the speeds of flame in cm./sec. given by mixtures obtained by mixing two primary mixtures A and B in various proportions.

Original temperature of mixtures 16° ± 3°.

A =		5·2% CS_2	4·5% CS_2	4·25% CS_2	4·25% CS_2	4·25% CS_2	3·5% CS_2	2·95% CS_2
B =		4·3% C_2H_2	9·0% CH_4	3·86% C_2H_2	3·35% Et_2O	2·29% n-C_5H_{12}	7·35% CH_4	6·6% CH_4
% A.	% B.							
100	0	80·3	63·5	57·9	57·7	57·7	40·6	31·2
95	5				39·3	37·2		23·5
92	8							19·5
90	10	70·8	46·4	44·8	33·1	33·0	27·4	no prop.
80	20				30·8		18·2	,,
75	25	64·7	40·2	37·5	30·6	30·8		
70	30						no prop.	
65	35		39·5					,,
60	40			38·4			,,	,,
50	50	62·7	42·5	41·0	34·9	36·8	21·8	
40	60		46·6	43·6		40·2	24·5	
35	65							,,
30	70							19·5
25	75	68·4	53·1	49·6	45·3	46·4		
20	80							23·0
15	85		57·1		50·4	51·2		
10	90						36·5	
0	100	79·8	63·5	58·5	58·1	58·0	40·5	31·0

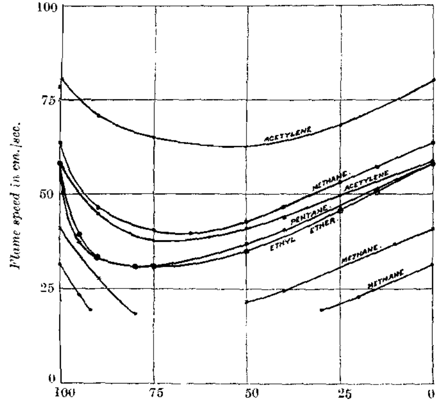
A =		14% CS_2	16·4% CS_2	19% CS_2	23·6% CS_2	6·48% CS_2	6·48% CS_2
B =		3·25% n-C_5H_{12}	10·7% CH_4	11·5% CH_4	12·17% CH_4	9·41% CH_4	2·53% n-C_5H_{12}
% A.	% B.						
100	0	74·6	61·4	49·8	37·0	109	109
95	5	47·2					
85	15	34·6				85·8	
80	20				27·7		
75	25	31·8	35·9	31·9			66·9
70	30				25·0		
69	31					69·6	65·5
50	50	28·8	26·3	24·4	21·6	57·5	60·8
40	60	29·1			19·7		60·6
35	65					57·6	
30	70				no prop.		
25	75	34·4	23·0	20·5		58·0	61·4
15	85	48·3				58·9	
10	90	58·0	27·5	20·8	no prop.		
5	95		38·5	25·5	20·3		
2·5	97·5				23·9		
0	100	74·9	61·0	50·1	37·2	66·0	70·5

containing only one combustible; (2) this effect appears to be rather more pronounced for mixtures containing a deficit of oxygen. For mixtures containing excess of oxygen the effect is best seen when the disulphide–air mixture is in excess, but with deficit of oxygen methane–air mixtures give the lowest speeds when the amount of added disulphide–air is small.

The curves shown for the blending of primary mixtures having flame speeds of about 58 cm./sec. are interesting. For mixtures containing little but carbon disulphide-air, the pentane curve shows lower speeds than that for ethyl ether, whilst the opposite appears to be the case when the complex mixture contains less than 75% of the disulphide-air. This appears to be due to the fact that, whereas pentane hinders the burning of the disulphide more than ether under these conditions, the pentane mixture contains an excess of oxygen, and the ether mixture is balanced for perfect combustion.

FIG. 5.

Flame speeds of mixtures obtained by blending CS_2-air mixtures containing excess oxygen with similar mixtures of other combustibles of the same flame speed.



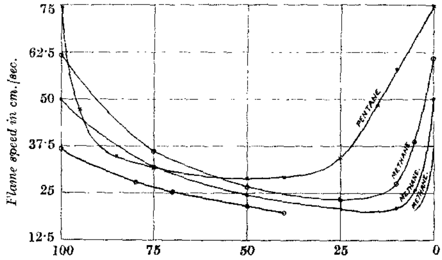
% of carbon disulphide–air mixture in complex mixture.

The sensitiveness of carbon disulphide mixtures to oxygen content at the lower limit has been emphasised in a previous communication (*loc. cit.*). Experiments still proceeding show that carbon disulphide mixtures appear to be abnormally sensitive to the oxygen content of the mixture. Thus the replacement of 20% of the nitrogen in a 4·5% mixture of the disulphide in air by oxygen caused an increase in flame speed very much greater than that caused in a methane–air mixture of similar oxygen excess under the same conditions. This also explains the relatively small lowering of flame speed caused by the acetylene–air mixture, which contains almost twice as much

oxygen as is required for complete combustion. The order of effectiveness of the substances here considered in hindering the burning of carbon disulphide would appear to be: *n*-pentane, ethyl ether, acetylene, methane. This agrees well enough with the author's list for effectiveness in hindering propagation at the lower limit, but disagrees with Dixon's order for effectiveness in raising the ignition temperature of carbon disulphide mixtures, which showed acetylene as being far more effective than ethyl ether (*Rec. trav. chim.*, 1925, 44, 305). This is possibly due to the fact that Dixon dealt largely with the preliminary phosphorescent combustion of carbon disulphide, a phenomenon far more closely allied to the slow "cool" flames

FIG. 6.

Flame speeds of mixtures obtained by blending CS_2–air mixtures having a deficit of oxygen with similar mixtures of other combustibles of the same flame speed.



discussed on p. 754 than to the ordinary burning of carbon disulphide; whether at the limit or not. It has been mentioned that these cool flames give rise to ordinary flames under certain conditions. It appears possible that under limiting temperature conditions the slow ignition of carbon disulphide–air or –oxygen mixtures would generally take place through this cool flame, in which the reactions probably differ considerably from those in the ordinary flame.

Carbon Disulphide Mixtures and the Law of Flame Speeds.

Payman and Wheeler have enunciated a generalisation which they have called the "Law of Flame Speeds," and have deduced from it conclusions which, if true, would be of the greatest importance. This law states: "If a complex mixture is made by blending a number of mixtures of air with simple combustible gases all of

which have the same speed of uniform movement of flame, then this complex mixture will also have the same speed of flame provided that all the mixtures are of the same type, all containing excess of oxygen or all containing excess of inflammable gas " (*Trans. Faraday Soc.*, 1926, **22**, 304). It is asserted that, by a slight extension of this, all flame speeds in complex mixtures may be calculated from those in mixtures containing only single combustible gases. Le Chatelier's rule for limit mixtures is stated to be a special case of this law (*loc. cit.*, p. 322), and it is also stated that examination of the exceptions to the Le Chatelier formula shows that the limiting speed of one of the inflammable gases is abnormally low. This does not appear to be necessarily so, for the limiting speed for carbon disulphide in air at the lower limit is seen to be the fairly normal value of 18·1 cm./sec., a figure identical with that quoted by Payman for ethane (J., 1919, **115**, 1444); yet in papers previously cited it has been shown that, although carbon disulphide was tested with 15 different combustibles, in no single instance did the mixtures follow Le Chatelier's rule. On the other hand, Payman and Wheeler (*ibid.*, p. 39) give the lower limiting speeds for hydrogen and methane in 9 mm. tubes as 8·3 and 32·6 cm./sec. respectively, and the observed lower limit is quoted as identical with that calculated. It thus appears likely that it is not the limiting speed, but the *type* of combustion occurring at the limit that determines whether a given pair of mixtures obeys Le Chatelier's rule or not.

Bone (*loc. cit.*, p. 420) has criticised some of the experimental work on which the law of speeds is based, and states, with reference to his own experimental work: " In none of the series have the requirements of the supposed ' law ' been fulfilled. . . ." He concludes that Payman and Wheeler's generalisation is not generally applicable to gaseous explosions.

The results in Figs. 5 and 6 form an excellent test of the applicability of the law to combustible–air mixtures containing carbon disulphide. Had the law held, all the curves shown there would have consisted of straight lines joining the speed values for the primary gas mixtures. The speeds of the complex mixtures are seen to be often less than one-half of their calculated values, and by blending primary mixtures of flame speeds less than about 40 cm./sec. it is generally possible to obtain mixtures that cannot propagate flame. The perfect combustion mixtures (last two mixtures of Table III) also give results at variance with speed-law predictions. A final test of the utility of the speed law in connexion with carbon disulphide was made when a complete speed–percentage composition curve was determined for air mixtures containing 3 vols. of carbon

disulphide to one of light petroleum as combustible. The results are in Table IV (where L.P. denotes light petroleum) together with similar determinations for light petroleum–air. The results calculated from the light petroleum–air and carbon disulphide–air results by speed-law methods are also given for comparison with those interpolated from the experimental speed–percentage curve. The calculated results are seen to be very different from the experimental values—the error is often over 100%—and an examination of Fig. 2, where the values are plotted for comparison with those of carbon disulphide, shows that the speed law is not applicable to carbon disulphide–air mixtures. As stated by the author (*Nature*, 1927, **119**, 51), the law of speeds must break down when one of the combustibles in a complex mixture interferes with the burning of another. Such interference is certainly partly responsible for the failure of the law of speeds in the case of carbon disulphide.

TABLE IV.

Showing the flame speeds in cm./sec. in mixtures of air with (*a*) light petroleum (L.P.) and with (*b*) a combustible consisting of 1 vol. of light petroleum to 3 vols. of carbon disulphide (gaseous); also (*c*) the speed-law results for the second series compared with interpolated values.

Original temperature of mixtures, 15° ± 2°.

(*a*)		(*b*)		(*c*)		
					Flame speed,	
% L.P.	Flame *speed.*	% of $3CS_2$ + 1 L.P.	Flame speed (*determined*).	% of $3CS_2$ + 1 L.P.	inter-*polated.*	calc. from *speed law.*
1·45	15·8	3·0	19·5	2·28	—	27·1
1·60	27·1	3·1	22·6	3·15	24·0	50·0
1·70	33·0	3·5	33·1	4·00	46·6	74·8
1·75	36·1	4·0	46·6	4·48	57·4	89·3
1·80	39·0	4·5	57·8	5·43	64·5	103
2·00	50·0	5·0	65·1	7·37	30·4	74·5
2·25	63·7	5·2	66·0	8·93	23·0	51·8
2·50	74·8	5·5	63·7	10·98	—	32·7
2·75	80·8	6·0	56·4	12·75	—	25·8
3·00	76·9	6·5	43·5			
3·25	65·3	7·0	33·6			
3·50	51·8	8·0	27·6			
3·75	41·0	9·0	22·7			
4·00	33·3					
4·60	25·8					

The light petroleum curve in Fig. 2 brings out a defect in the enunciation of the law of speeds. The position of the mixture for perfect combustion (containing 2·32% of the combustible) lies on the straight portion of the curve to the origin side of the maximum.

By blending two mixtures of equal speed, both deficient in oxygen but corresponding to two points one on each side of the maximum, in any proportion whatsoever, the resulting mixture must show a higher flame speed. In the case of light petroleum, this increase may amount to 20% of the value of the speed of the primary mixtures. Again, when one of these primary mixtures is blended with an oxygen-deficient mixture of the same speed containing another combustible, the speed of the blended mixture will evidently depend on which of the two available light petroleum mixtures has been used.

It has previously been shown that at the lower limit, in particular, the effect caused by adding a second combustible to carbon disulphide reached a maximum, after which the vapour behaved quite normally and gave results corresponding closely to those expected from its calorific value. A similar effect can be traced when other combustible–air mixtures are added progressively to those of carbon disulphide. For example (considering the 58 cm./sec.-mixture curves in Fig. 5), the first effect of the added mixture is to cause a pronounced fall in speed, but this effect decreases as more of the second mixture is added, and ultimately gives place to a steady rise to the speed value of the second mixture. The straight portion on the right of the curve becomes less pronounced for mixtures of higher speeds and could hardly be distinguished for the perfect combustion mixtures. It is shown clearly by only one of the curves for mixtures deficient in oxygen. Its presence in those for medium speed mixtures having an oxygen excess, however, indicates that the second combustible has practically attained a steady maximum effect in hindering the burning of the disulphide, and the slope of the line indicates that the disulphide mixtures are behaving as if they possessed a far lower flame speed than that experimentally determined for them. A rough idea of the effective speed of these mixtures in the presence of an excess of another combustible can probably be obtained by producing the sloping straight line to cut the 100% carbon disulphide mixture axis. When this is done, it seems that in the presence of excess of methane mixture having the same flame speed, the disulphide mixture, having a flame speed of 63·5 cm./sec. when burning alone, behaves as if its flame speed were about 21 cm./sec., whereas under similar conditions, one having a speed of 40·6 cm./sec. behaves as if its flame speed were zero. These figures, however, can have little absolute significance, for what may be termed the effective speed in complex mixtures of the 58 cm./sec. carbon disulphide–air mixture seems to vary from about 7 to about 21 cm./sec., depending upon whether the inhibiting combustible is

ethyl ether or acetylene. This difference is almost certainly due to the great difference in oxygen content between the two mixtures of these combustibles used. The abnormal sensitiveness of the speed of flame in carbon disulphide mixtures to changes in their oxygen content supplies a second cogent reason for the non-applicability of the speed law to mixtures containing carbon disulphide, and the fact that certain mixtures propagate stable flames at uniform, but widely different, speeds rather tends to discount any law based on flame speeds alone.

The results obtained make it fairly certain that the burning of carbon disulphide in air is catalysed, probably by some product of its combustion, and that this catalysis is inhibited by the presence of material quantities of any one of a large number of other combustibles. It is hoped to extend this work to detonation phenomena in carbon disulphide mixtures.

Summary.

(1) Flame-speed determinations under uniform movement conditions have been made for carbon disulphide–air and carbon disulphide–second combustible–air mixtures.

(2) Certain carbon disulphide–air mixtures have two widely differing flame speeds producible at will by varying the conditions of ignition. These two types of flame, cool and ordinary, give different lower limits.

(3) The presence of certain other combustibles hinders the burning of carbon disulphide in air throughout its propagation range.

(4) Flame speeds in dilute carbon disulphide–air mixtures are far more sensitive to oxygen content than in similar mixtures of normal combustibles.

(5) The law of flame speeds is not applicable to mixtures containing carbon disulphide.

(6) It is concluded that the normal burning of carbon disulphide in air is catalysed.

I wish to thank Messrs. Nobel Industries, Ltd., and particularly Mr. Rintoul, manager of the Research Section, for facilities accorded me for carrying out this work.

THE NOBEL LABORATORIES,
ARDEER. [*Received, January 21st*, 1928.]

Spectra and Atoms.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY ON FEBRUARY 23RD, 1928.

By A. FOWLER, D.Sc., F.R.S., Yarrow Research Professor of the Royal Society.

*ONE of the chief purposes of present-day spectroscopy is the correl*ation of the structure of spectra with the structure of atoms. The possibility of such a correlation was clearly in the minds of some of the earlier workers in spectroscopy, but nothing very definite emerged until the advent of the Rutherford-Bohr theory nearly fifteen years ago. Meanwhile, however, substantial progress had been made in disentangling the structure of the spectra themselves.

The spectra of most of the elements are very complicated—some containing thousands of lines—and it was only by reducing them to simpler terms that there could be any hope of finding a theoretical interpretation. Fortunately, the spectra of a few of the elements are relatively simple, and it was the study of these that paved the way to the quantum theory of spectra and afterwards to the elucidation of the more complex spectra.

The earlier investigations were primarily directed to the identification of regular *series* of lines which could be represented by simple formulæ. Such a series, as exemplified by the well-known Balmer series of hydrogen and the arc spectra of the alkali metals, consists of a number of lines of gradually diminishing intensity, and diminishing distance apart in passing to shorter wave-lengths, and each series approaches a definite limit. Near the limit the lines become very closely crowded together, but no series has actually been observed to its limit. Rydberg's original formula represents lines of a series with sufficient accuracy for our present purposes, namely,

$$\nu = A - R/(m + \mu)^2.$$

Here ν represents the wave-numbers of the series lines corresponding to successive integral values of m; A is the wave-number of the limit ($m = \infty$); R is the "Rydberg constant" ($= 109678$ as calculated from the hydrogen series); and μ is a constant (usually a fraction) special to each series and determined, together with A, from the observed lines. Each line of a series is thus represented by the difference of two terms.

Different types of series were early recognised. In the alkali spectra, that which includes the strongest lines was called the Principal series; the next brightest, consisting of somewhat diffuse lines, was called the Diffuse series; and another was called the Sharp series in consequence of the frequent occurrence of sharply-defined lines in series of this type. Other types of series were afterwards recognised, only one of which, however —the badly-named Fundamental series—has received a special designation.

The work of Rydberg showed that the various series in the same spectrum were closely related to one another, and this naturally brought about a considerable simplification in the mode of representing them. For example, the limiting term A in the formula for a given series is also a term of one of the associated series. The word "*term*" has thus come to have a special meaning in spectroscopy, representing something quite different from the spectrum lines themselves. The wave-number of a spectrum *line* always appears as the difference of two *terms*, and in attempting to analyse the structure of a spectrum we are really trying to find out the spectroscopic terms from which it is built up.

The consideration of these matters is greatly facilitated by the use of an abbreviated notation. The initial letters of the names previously assigned to the actual series are now universally adopted for the respective sequences of terms. If the first member of each term sequence be denoted by 1, we have

Principal	series	$= 1S - mP$
Sharp	,,	$= 1P - mS$
Diffuse	,,	$= 1P - mD$
Fundamental	,,	$= 1D - mF$
FG	,,	$= 1F - mG$, etc.

It is to be understood that $1S$, for example, means the first term of the S sequence, whereas mS represents a regular sequence of terms ($1S$, $2S$ . . .), and that a *sequence* of terms in combination with the first term of another sequence gives rise to one of the main series of lines.

Ritz was the first to recognise clearly, as expressed in the "Combination Principle," that other terms besides the first of a sequence might combine with terms from other sequences to produce spectrum lines; as, for example, $2S - mP$. The possible combinations, however, are not so numerous as Ritz appears to have thought; they are restricted by certain selection rules, which

will be stated more fully a little later. Meanwhile, it will suffice to remark that if the term sequences are written in the order *S*, *P*, *D*, *F* . . ., the combinations which ordinarily occur in the simpler spectra are only those between terms indicated by adjacent letters.

It should be further observed that in some spectra all terms other than those of *S* type have two values (in most cases not very different), giving series consisting of doublets, as in the well-known spectrum of sodium. In other spectra, all terms except *S* have three values, giving rise to triplets. A combination of two doublet terms, however, does not give four lines, as might have been expected, but only three; and, similarly, a combination of two triplet terms yields only six of the nine lines which are arithmetically possible. Clearly, another selection principle comes into operation, and for its application it is necessary to distinguish the components of each multiple term by what are now called "inner quantum" numbers.

These early investigations showed, among other things, that the spectra of the alkali metals were all of similar character, but differed in the fact that corresponding lines were mostly displaced to longer wave-lengths with increase of atomic weight, and that the doublet separations increased roughly as the squares of the atomic weights. All elements of the second group were similarly found to exhibit singlet and triplet series, and here also the triplet separations were found to vary approximately as the squares of the atomic weights. In the third group the elements of the aluminium sub-group were found to be characterised by doublets.

The spectra of rather more than 20 elements had been wholly or partly resolved into series before the year 1913, when Bohr's theory came to illuminate the subject of spectral structure by its interpretation of spectroscopic terms as energy levels of the atom. On this theory, an excited atom can exist temporarily in certain "stationary" or non-radiating states, each of a definite energy value, and not in any intermediate state, the possible states being governed by quantum considerations. A spectrum line is to be regarded as representing the energy lost by an atom when it passes from one state of a certain energy to another of lesser energy. In its normal unexcited state, the atom is in the state of lowest energy, but it may pass to states of greater energy by the absorption of radiation or by collisions of certain types.

In terms of electron orbits, the spectrum of a neutral atom is supposed to be generated, one line at a time, by the migrations of the most loosely bound electron between the different orbits per-

mitted by quantum conditions, and the whole spectrum is the integration of the multitude of transitions going on in different atoms at the same time. This theory, I need scarcely remind you, accounted quantitatively for the spectrum of hydrogen and that of ionised helium, and in a general way for the series spectra of other elements.*

The energy representative of an orbit is, in the first place, dependent upon its size, and, in the simplest consideration, is the same whether the orbit be a circle or an ellipse having a major axis equal to the diameter of the circle. It was shown by Sommerfeld, however, that in consequence of the varying velocity of an electron in an elliptic orbit, and the consequent relativistic variation of its mass, the energies of orbits of different eccentricities, though having the same major axes, must be slightly different. It was in this way that he predicted the "fine structure" of the lines of the Balmer series of hydrogen. In more complex atoms, the migrating electron is subjected to a perturbing action arising from the presence of additional electrons, but here the effect is much greater than that due to relativity considerations, and gives rise to the separate series.

It thus became necessary to use two quantum numbers to define an electron orbit. They are written in the form n_k, where n is called the *principal quantum number* and k the *azimuthal quantum number*. In a rough approximation, n determines the major axis and k the minor axis of the ellipse, hoth being restricted to definite integral values.

In the earlier days of the theory it was supposed that only a single electron was involved in the production of the spectrum, and that the type of a spectroscopic term corresponded to the k value of the electron orbit in accordance with the scheme:

Term	S	P	D	F
k	1	2	3	4

For example, if the largest spectroscopic term, or "ground term," in a spectrum was found to be of P type, it was supposed that the electron last added in the formation of the atom occupied an orbit for which $k = 2$. Or if the atom was excited, and the series electron occupied a 3_2 orbit, the corresponding term would be $3P$. It will be noted that the selection rule previously mentioned is equivalent

* The orbital picture of atomic structure is adopted for convenience of description, but it should be understood that this may not represent the final interpretation.

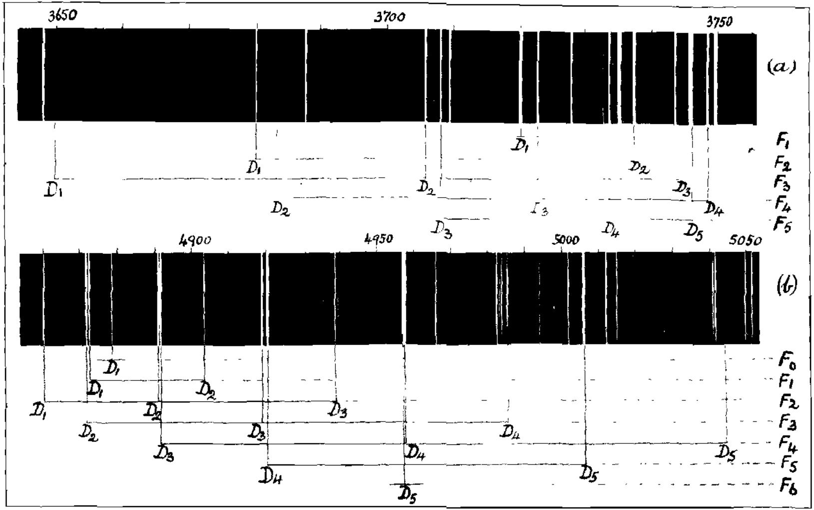
to stating that an electron can only change from one orbit to another for which k differs by ± 1. All this was in entire agreement with the spectroscopic data then available.

From the spectroscopic data, considering also the general chemical and physical properties of the elements, Bohr built up his well-known table (1922) showing the probable distribution of the electrons in n_k groups in the atoms of a considerable number of elements. These ideas of Bohr have been modified in certain details, and remarkably extended in recent years, so that it has become possible to specify with certainty the electron arrangements for the great majority of the elements and the most probable arrangement for the remainder. These developments have been made possible by advances in the analysis of complex spectra and in the general theory.

The key to the structure of the more complex spectra was furnished, in 1922, by Catalán, who was then working in my laboratory at the Imperial College. Up to that time the search for regularities in spectra had been mainly guided by the idea of extended regular series of lines, and definite results had only been obtained for about one-quarter of the chemical elements. Singlet, doublet, and triplet terms were all that were then known, but in his work on manganese and a few other elements, Catalán discovered complex groups of related lines which involved terms of higher multiplicities. Sommerfeld soon afterwards showed how the scheme of inner quantum numbers which he had devised for the simpler terms could be extended to the new multiplicities, and the identification of what Catalán had called " multiplets " in numerous spectra rapidly followed. Strictly speaking, of course, the name *multiplet* is applicable to all combinations of spectroscopic terms other than those of a singlet system.

Many spectra which had previously defied analysis have thus been found to be built up chiefly of complicated multiplets, each of which can be represented by taking differences between two multiple terms, subject to appropriate selection rules. The same multiple term may be involved in several multiplets, but Rydberg sequences extending to more than two or three consecutive terms are infrequent.

The discovery of higher multiplicities has necessitated considerable extension of the notation for spectroscopic terms. The term types being represented by their original symbols, the multiplicity (r) of the system to which a term belongs is indicated by a numerical superscript on the left of the symbol, and the inner quantum number by a subscript on the right; as ${}^3P_2$, ${}^5F_4$, and so on. A term itself



Multiplets in the arc spectrum of iron. (a) = $^5D^5F$. (b) = $^7D^7F$.

[To face page 769.]

is distinguished from others of the same type in various ways, and there is, as yet, no general agreement on this point. Examples will appear in due course.

The inner quantum numbers (j), which play so large a part in determining the permissible combinations, are indicated in the following table:

Inner Quantum Numbers (j).

Odd Multiplicities.

Terms	L.	Singlet $r = 1$.	Triplet $r = 3$.	Quintet $r = 5$.	Septet $r = 7$.
S	0	0	1	2	3
P	1	1	0 1 2	1 2 3	2 3 4
D	2	2	1 2 3	0 1 2 3 4	1 2 3 4 5
F	3	3	2 3 4	1 2 3 4 5	0 1 2 3 4 5 6
G	4	4	3 4 5	2 3 4 5 6	1 2 3 4 5 6 7

Even Multiplicities.

Terms	L.	Doublet $r = 2$.	Quartet $r = 4$.	Sextet $r = 6$.	Octet $r = 8$.
S	0	1	2	3	4
P	1	1 2	1 2 3	2 3 4	3 4 5
D	2	2 3	1 2 3 4	1 2 3 4 5	2 3 4 5 6
F	3	3 4	2 3 4 5	1 2 3 4 5 6	1 2 3 4 5 6 7
G	4	4 5	3 4 5 6	2 3 4 5 6 7	1 2 3 4 5 6 7 8

The values here assigned to the inner quantum numbers are not only in empirical accordance with the actual spectroscopic observations, but now have a theoretical basis. When two multiple terms enter into combination to form a multiplet, lines appear only when the j values differ by unity or zero; *i.e.*, $\Delta j = \pm 1$ or 0; also, a transition 0 to 0 is never found. It will readily be seen, for example, that a combination of a ^3D with a ^3P term will give six, and not nine, lines.

Terms of different multiplicities occur in most spectra, but in a given spectrum all the terms are either all odd or all even. Inter-system combinations, still subject to the j condition, only occur for systems in which $\Delta r = \pm 2$.

The two multiplets from the arc spectrum of iron which are shown in Plate I will illustrate the application of the inner quantum selection rule. The first shows a quintet D in combination with a quintet F term, and the second a corresponding combination of septet terms. The lines selected from the far greater number among which they appear are justified by the following schemes of wave-number differences:

	$^5D_0$.		$^5D_1$.		$^5D_2$.		$^5D_3$.		$^5D_4$.
$^5F_1$	26688·31	*89·91*	26778·22	*184·11*	26962·43				
			106·77		*106·76*				
$^5F_2$			26671·45	*184·12*	26855·57	*288·03*	27143·66		
					164·88		*164·90*		
$^5F_3$					26690·69	*288·07*	26978·76	*415·91*	27394·67
							227·88		*227·85*
$^5F_4$							26750·88	*415·94*	27166·82
									292·29
$^5F_5$									26874·53
	$^7D_1$.		$^7D_2$.		$^7D_3$.		$^7D_4$.		$^7D_5$.
$^7F_0$	20493·53								
	25·55								
$^7F_1$	20519·08	*130·43*	20388·65						
	52·41		*52·34*						
$^7F_2$	20571·49	*130·50*	20440·99	*198·91*	20242·08				
			81·55		*81·56*				
$^7F_3$			20522·54	*198·90*	20323·64	*271·30*	20052·34		
					114·26		*114·26*		
$^7F_4$					20437·90	*271·30*	20166·60	*347·51*	19819·09
							150·80		*150·85*
$^7F_5$							20317·40	*347·46*	19969·94
									195·44
$^7F_6$									20165·38

Other types of terms, H, J, K . . ., are found in some spectra, but the number of components of a term never exceeds the maximum indicated by the name of the system to which it belongs.

One result of great significance arising out of the analysis of these complex spectra was that the largest spectroscopic term—representing the normal state of the atom in question—was sometimes of a type which could not possibly be regarded as showing the k value of the last-bound electron. For example, the "ground term" of titanium (22) is of the type ^3F, and on the simple theory this would require the last electron to be bound in a 4_4 orbit. This would place it far beyond all the other electrons, in an orbit which it would be very unlikely to occupy unless in an excited state.

The original theory, in fact, left other details unexplained, even in connexion with atoms which had been considered comparatively simple. For instance, in copper there are many lines of the arc spectrum which are not included in the system of doublets. Again, in the alkaline earths there are groups of lines (known to spectroscopists as PP', DD', etc., multiplets) which are not included in the regular triplet series, although involving some of the ordinary triplet terms.

The next great advance in the theory of spectra arose out of an investigation by Russell and Saunders of such groups of lines in the arc spectrum of calcium. Some of the new triplet terms involved in these groups, which apparently violated the familiar selection rule for k, were found to represent greater amounts of energy than that necessary to drive a single electron completely out of the atomic system. Russell and Saunders were thus forced to the conclusion that in some of the atoms of calcium a second electron was displaced while the first still remained within the system and that the emission represented the combined energies due to simul-

taneous jumps of both electrons to smaller orbits. The quantum numbers which defined the spectroscopic terms could therefore no longer be identified with those which specified the orbit of a single electron. Consequently, the spectroscopic terms have now to be defined by "group quantum" numbers, representing a kind of resultant of the k orbital numbers. These new numbers are mostly represented by L, which equals 0, 1, 2 . . . for S, P, D . . .

Arising out of this brilliant new idea in the theory of spectra, to which important contributions were also made by Pauli and Heisenberg, a complete scheme has been developed by Hund whereby the types of spectroscopic terms corresponding to any specified arrangement of the electrons in n_k orbits can be calculated. Or, conversely, the orbital numbers can be indicated when the terms have been identified. There is no time to explain how this is done, but I may say that the results given by the theory have been abundantly confirmed by the recent analyses of many complex spectra. The whole theory is based upon the assumption that an atom is so constituted that the angular momenta of all its rotary motions can only change by unit steps, the unit being $h/2\pi$. It gives a physical meaning to the inner quantum numbers by identifying them with the resultant angular momenta of the entire atom in its various possible quantised states.

The new theory has also an important bearing on the theory of the Periodic System in virtue of Pauli's principle, which forbids more than one electron to occupy an orbit having the same four quantum numbers now necessary to define the motions completely. One of the new quantum numbers involves the orientation of the orbit, and the other the orientation of spin of the electron; they are called magnetic quantum numbers.

Pauli's principle of exclusion at once leads to a modification of Bohr's original distribution of electrons in n_k sub-groups, identical with that to which Main Smith and Stoner had been led independently, chiefly by the consideration of chemical and physical properties respectively. In the new scheme, the inner sub-levels have fewer electrons and there is a greater concentration in the outer sub-levels of each n_k group. The spectroscopic theory, however, does not give the distribution of electrons in all the X-ray sub-levels, but only the arrangement in n_k sub-groups. It results from the theory that the maximum number in any of these sub-groups is given by $4k - 2$, in agreement with Main Smith and Stoner. There are accordingly strong theoretical foundations for the new table of electron arrangements. It has not yet been confirmed for every element by spectroscopic methods, but this seems to be merely a question of time.

Table of Atomic Structures.

Element	Atomic Number	K	L		M			N				O (Extra-nuclear Electronic Configurations.)					P						Q		
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2	7_3
H ...	1	1																							
He ...	2	2																							
Li ...	3	2	1																						
Be ...	4	2	2																						
B	5	2	2	1																					
C	6	2	2	2																					
N	7	2	2	3																					
O	8	2	2	4																					
F	9	2	2	5																					
Ne ...	10	2	2	6																					
Na ...	11	2	2	6	1																				
Mg ...	12	2	2	6	2																				
Al ...	13	2	2	6	2	1																			
Si ...	14	2	2	6	2	2																			
P	15	2	2	6	2	3																			
S	16	2	2	6	2	4																			
Cl ...	17	2	2	6	2	5																			
A	18	2	2	6	2	6																			
K ...	19	2	2	6	2	6		1																	
Ca ...	20	2	2	6	2	6		2																	
Sc ...	21	2	2	6	2	6	1	2																	
Ti ...	22	2	2	6	2	6	2	2																	
V	23	2	2	6	2	6	3	2																	
Cr ...	24	2	2	6	2	6	5	1																	
Mn ...	25	2	2	6	2	6	5	2																	
Fe ...	26	2	2	6	2	6	6	2																	
Co ...	27	2	2	6	2	6	7	2																	
Ni ...	28	2	2	6	2	6	8	2																	
Cu ...	29	2	2	6	2	6	10	1																	
Zn ...	30	2	2	6	2	6	10	2																	
Ga ...	31	2	2	6	2	6	10	2	1																
Ge ...	32	2	2	6	2	6	10	2	2																
As ...	33	2	2	6	2	6	10	2	3																
Se ...	34	2	2	6	2	6	10	2	4																
Br ...	35	2	2	6	2	6	10	2	5																
Kr ...	36	2	2	6	2	6	10	2	6																
Rb ...	37	2	2	6	2	6	10	2	6			1													
Sr ...	38	2	2	6	2	6	10	2	6			2													
Y	39	2	2	6	2	6	10	2	6	1		2													
Zr ...	40	2	2	6	2	6	10	2	6	2		2													
Nb ...	41	2	2	6	2	6	10	2	6	4		1													
Mo ...	42	2	2	6	2	6	10	2	6	5		1													
Ma ...	43	2	2	6	2	6	10	2	6	6		1													
Ru ...	44	2	2	6	2	6	10	2	6	7		1													
Rh ...	45	2	2	6	2	6	10	2	6	8		1													
Pd ...	46	2	2	6	2	6	10	2	6	10															
Ag ...	47	2	2	6	2	6	10	2	6	10		1													
Cd ...	48	2	2	6	2	6	10	2	6	10		2													
In ...	49	2	2	6	2	6	10	2	6	10		2	1												
Sn ...	50	2	2	6	2	6	10	2	6	10		2	2												
Sb ...	51	2	2	6	2	6	10	2	6	10		2	3												
Te ...	52	2	2	6	2	6	10	2	6	10		2	4												
I	53	2	2	6	2	6	10	2	6	10		2	5												
Xe ...	54	2	2	6	2	6	10	2	6	10		2	6												
Cs ...	55	2	2	6	2	6	10	2	6	10		2	6				1								
Ba ...	56	2	2	6	2	6	10	2	6	10		2	6				2								

Extra-nuclear Electronic Configurations.

Element	Atomic Number	K	L		M			N				O					P						Q		
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2	7_3
La ...	57	2	2	6	2	6	10	2	6	10		2	6	1			2								
Ce ...	58	2	2	6	2	6	10	2	6	10	1	2	6	1			2								
Pr ...	59	2	2	6	2	6	10	2	6	10	2	2	6	1			2								
Nd ...	60	2	2	6	2	6	10	2	6	10	3	2	6	1			2								
Il ...	61	2	2	6	2	6	10	2	6	10	4	2	6	1			2								
Sa ...	62	2	2	6	2	6	10	2	6	10	5	2	6	1			2								
Eu ...	63	2	2	6	2	6	10	2	6	10	6	2	6	1			2								
Gd ...	64	2	2	6	2	6	10	2	6	10	7	2	6	1			2								
Tb ...	65	2	2	6	2	6	10	2	6	10	8	2	6	1			2								
Ds ...	66	2	2	6	2	6	10	2	6	10	9	2	6	1			2								
Ho ...	67	2	2	6	2	6	10	2	6	10	10	2	6	1			2								
Er ...	68	2	2	6	2	6	10	2	6	10	11	2	6	1			2								
Tu ...	69	2	2	6	2	6	10	2	6	10	12	2	6	1			2								
Yb ...	70	2	2	6	2	6	10	2	6	10	13	2	6	1			2								
Lu ...	71	2	2	6	2	6	10	2	6	10	14	2	6	1			2								
Hf ...	72	2	2	6	2	6	10	2	6	10	14	2	6	2			2								
Ta ...	73	2	2	6	2	6	10	2	6	10	14	2	6	3			2								
W ...	74	2	2	6	2	6	10	2	6	10	14	2	6	4			2								
Re ...	75	2	2	6	2	6	10	2	6	10	14	2	6	5			2								
Os ...	76	2	2	6	2	6	10	2	6	10	14	2	6	6			2								
Ir ...	77	2	2	6	2	6	10	2	6	10	14	2	6	7			2								
Pt ...	78	2	2	6	2	6	10	2	6	10	14	2	6	9			1								
Au ...	79	2	2	6	2	6	10	2	6	10	14	2	6	10			1								
Hg ...	80	2	2	6	2	6	10	2	6	10	14	2	6	10			2								
Tl ...	81	2	2	6	2	6	10	2	6	10	14	2	6	10			2	1							
Pb ...	82	2	2	6	2	6	10	2	6	10	14	2	6	10			2	2							
Bi ...	83	2	2	6	2	6	10	2	6	10	14	2	6	10			2	3							
Po ...	84	2	2	6	2	6	10	2	6	10	14	2	6	10			2	4							
EkaI	85	2	2	6	2	6	10	2	6	10	14	2	6	10			2	5							
Rn ...	86	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6							
EkaCs	87	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6					1		
Ra ...	88	2	2	8	2	6	10	2	6	10	14	2	6	10			2	6					2		
Ac ...	89	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	1				2		
Th ...	90	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	3				1		
U-X	91	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	4				1		
U ...	92	2	2	6	2	6	10	2	6	10	14	2	6	10			2	6	5				1		

The way in which the spectroscopic terms are now correlated with the electron configurations may be gathered from the relatively simple case of magnesium, as shown below.

Magnesium.

K	L		M			N					Terms.
1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4		
2	2	6	2							3*s*	^1S
2	2	6	1	1						3*p*	^1P ^3P
2	2	6	1		1					3*d*	^1D ^3D
2	2	6	1			1				4*s*	^1S ^3S
2	2	6	1				1			4*p*	^1P ^3P
2	2	6	1					1		4*d*	^1D ^3D
2	2	6		2						3*p′*	^1S ^1D ^3P
2	2	6		1	1					3*d′*	^1P ^1D ^1F ^3P ^3D ^3F

The table shows the arrangement of electrons in the neutral atom and in a number of excited states. The normal state, with two

electrons in 3_1 orbits, is represented by the singlet term ^1S. When one of the 3_1 electrons is excited to a 3_2 orbit, the corresponding terms are ^1P and ^3P; and so on. It should be remarked here that in deducing the terms, all n_k sub-groups which have their full quotas may be disregarded, as their angular momenta cancel out. Further, it should be explained that an n_k configuration may be represented by more than one spectroscopic term in consequence of the dependence of the energy, in part, on the orientation of the orbit and on that of spin of the electron.

In this case, when only one of the outermost electrons is displaced, the term types correspond with the k's of the electrons, as in the earlier theory. When two electrons are displaced in the way shown in the lower part of the diagram, new terms arise for which the types are no longer directly indicated by the k of an electron. The type is now related to the quantised vectorial sum of the k values of the individual electrons. The selection rules have accordingly to be transferred from the terms to the electrons. Combinations between terms arising from different configurations can occur only when k changes by ± 1 for one electron and by ± 2 or 0 for the other, it being supposed that not more than two electrons make simultaneous jumps.

Thus, in magnesium, the terms $3p'^1S$, etc., may combine with $3p^1P$, $3p^3P$, but not with $3d^1D$, $3d^3D$; $3d'^1P$, etc., may combine with $3p'^1S$, etc., or with $3d^1D$, but not with $3p^1P$. Combinations between terms in the upper part of the table, always subject to inner quantum restrictions, give the series which were long ago recognised by Rydberg and by Kayser and Runge; and combinations between the rows of terms in the lower part, or of these with selected rows of terms in the upper part, give multiplets of the kind discussed by Russell and Saunders.

It will be interesting to survey the spectra of some of the elements in relation to the new table of atomic structures. In general elements in which the incompletely filled n_k sub-groups have the same number of electrons—the completely occupied sub-groups "cancelling out"—give spectra of similar character. Thus, the similarity of the spectra of the alkali metals, all of which consist of doublets, arises from the fact that there is only a single electron lying outside completed sub-groups. The spectra of Cu, Ag, and Au of Group I also include doublet series, but some interesting points in connexion with these may be more conveniently considered later.

As will be seen on reference to the table, all elements of Group II have two electrons in n_1 orbits, and all the underlying sub-groups of orbits, if occupied at all, are completed. We have already seen

that the spectra of all these elements are of similar character, consisting of singlets and triplets.

In boron and the aluminium sub-group of elements there is only a single n_2 electron outside closed n_k sub-groups, and the spectra are again characterised by doublets. Odd and even multiplicities, in fact, alternate without exception right across the columns of the periodic table.

The spectra of the scandium sub-group of Group III are of exceptional interest, inasmuch as, though showing even multiplicity, they are very different from those of the aluminium sub-group in other respects. Here, *in the normal atom*, we observe that *all the occupied n_k sub-groups are completely filled with the exception of the n_3 orbits.* In scandium, the 3_3 sub-group contains only one electron and accordingly gives ^2D for the ground term, as compared with ^2P in aluminium. The continuity of the electron configurations for successive atoms is first interrupted at potassium, where the 19th electron occupies a 4_1 in preference to a 3_3 orbit. That this must be so is certainly indicated by the potassium spectrum, and it follows that at this stage the last added electron is more firmly bound in 4_1 than in 3_3. The same is true when the 20th electron also goes into a 4_1 orbit in the formation of the calcium atom. But when the 21st electron is added to form the scandium atom, it is most firmly bound in a 3_3 orbit.

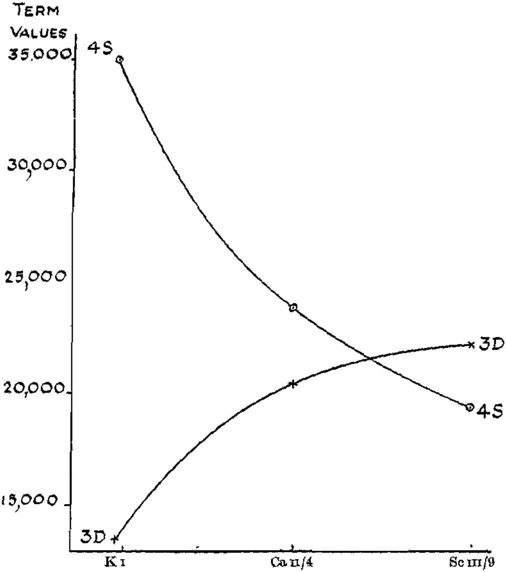
In compiling his original table, showing this arrangement for scandium, Bohr argued from a comparison of the spectrum of potassium (K I) with the similar spectrum of ionised calcium (Ca^+ or Ca II), for both of which the spectroscopic terms were known. As shown in the appended diagram,* it was clear that as the nuclear charge increased, the $3D$ term was tending to approach the $4S$ term in magnitude, and Bohr inferred that in doubly-ionised scandium (Sc^{++} or Sc III) the $3D$ term would be the largest. This has lately been verified experimentally by Russell, whose results for Ti IV also provide further confirmation.

This change in the electron structure at Sc is naturally accompanied by a change in the character of the spectrum and in the chemical properties of the element, as compared with Al, which also has three outer electrons, but arranged differently.

The filling up of the 3_3 orbits continues from Sc to Ni in the way shown in the table, forming the first transition group of elements. All their spectra are very complicated, but the main features of their structures have been determined and completely verify the normal electron arrangements specified for them.

* As usual in such comparisons, the terms of Ca II have been divided by 4 and those of Sc III by 9.

The second set of transition elements, Y to Pd, is similarly marked by the filling up of the 4_3 sub-group, but the order of filling up, which has also been confirmed by the analyses of the spectra, is not exactly the same. Thus, whereas Ni (28), marking the end of the first set, has eight 3_3 and two 4_1 electrons, the end of the second set is marked by Pd (46) with ten 4_3 electrons. The Pd atom thus



has all its occupied sub-groups completely filled, more or les resembling a rare gas, and is consequently very stable. The groun term of Pd is accordingly a ^1S term, whereas that of Ni is a ^{3} term.

The effect of this difference is seen when the next consecutiv elements are respectively formed by the addition of another electro In the case of Ag (47), which follows Pd, the added electron fal into a 5_1 orbit, and its spectrum is of the simple alkali typ

consisting of doublet series; and the simplicity of the spectrum, it will be observed, is matched by the simple univalence of silver.

On the other hand, the arc spectrum of Cu (29), which follows Ni, gives many lines in addition to those of the alkali type which depend on a single electron outside completed n_k groups. In consequence of the tendency of Cu to approach the Ni configuration, a system of nine 3_3 and two 4_1 electrons is nearly as stable as one having ten 3_3 and one 4_1. Two electrons are thus liable to displacement, and it is in this way that the added complexity of the Cu spectrum, as compared with Ag, is accounted for. Presumably, this also accounts for the two valencies of copper.

The general outcome of such investigations, which I cannot pursue further for want of time, is to show, not only the beautifully systematic character of atom-building, but also that all the main features of the spectrum of an atom, however complex, can now be theoretically predicted if the electron configurations are known. Or, conversely, from a knowledge of the spectroscopic terms the corresponding configurations of electrons can be correctly deduced.

So far, I have dealt chiefly with the spectra of neutral atoms, but the spectra of ionised atoms are also of great importance as supporting the general theory. Bohr's theory, in the first instance, was greatly strengthened by its extension from hydrogen to ionised helium, the spectrum of which was already known from my own observations, though its origin had previously been misunderstood. When one electron has been entirely removed by the exciting agency, the helium atom resembles that of hydrogen, except that the mass of the nucleus is four times as great and its positive charge twice as great. It follows that the lines of ionised helium should be given, in a first approximation, by the same formula as that for hydrogen, except that the Rydberg constant, R, must be replaced by $4R$. Actually, a slight difference between R_H and R_{He} (= 109678 and 109722, respectively) was fully explained by taking account of the difference in mass of the respective nuclei, which does not otherwise affect the spectrum. Subsequent investigations showed that the value $4R$ was characteristic of the series lines of singly-ionised atoms generally, so that a spectrum arising from such atoms could be certainly identified as such if $4R$ appeared in the formula representing its series lines.

Bohr further foresaw that if an atom has lost two electrons, the remainder, or "core," of the atom must have a double positive charge with respect to the migrating electron, and that the series lines would be characterised by $9R$. If three electrons had been removed so that the atom was trebly-ionised, the series constant would become $16R$; and so on. These expectations were, in the

first instance, most completely verified by Paschen's work on Al III and my own work on Si IV, the spectra being produced by the action of strong discharges. Here the observational data were ample for the calculation of the series constants, and Bohr's predictions were fully established.

When atoms resemble each other in everything but nuclear charge and mass, they are said to be "iso-electronic," and the relations between their spectra are beautifully simple. They are, of course, all of similar type, but corresponding lines are systematically displaced to shorter wave-lengths as the nuclear charge increases. The displacements in wave-numbers are, in fact, almost linear, in accordance with the "irregular doublet" law deduced by Sommerfeld for *X*-ray spectra. The separations in the doublets also increase systematically with higher atomic number in agreement with the "regular doublet" law of Sommerfeld. Comparing the iso-electronic atoms Na I, Mg II, Al III, Si IV, the following table will illustrate the simple relations in question.

	Na I.	Mg II.	Al III.	Si IV.
Wave-lengths	5,896 5,890	2,803 2,796	1,863 1,855	1,402 1,394
Wave-numbers.........	16,956 16,973	35,669 35,761	53,680 53,918	71,280 71,740
Separations	17	92	238	460

Many spectra have since been investigated, with similar results, even among more complex spectra, as shown, for example, by the work of Gibbs and White on the displacements and separations of corresponding multiplets in the spectra of Sc I, Ti II, and V III.

Special attention has been given by Millikan and Bowen, and by myself, to elements in the first row of the periodic table. All the possible states of these atoms are included in the following scheme:

Series constant.	Atomic no. 1.	2.	3.	4.	5.	6.	7.	8.	9.
R	H	He I	Li I	Be I	B I	C I	N I	O I	F I
$4R$	He II	Li II	Be II	B II	C II	N II	O II	F II	
$9R$	Li III	Be III	B III	C III	N III	O III	F III		
$16R$	Be IV	B IV	C IV	N IV	O IV	F IV			
$25R$	B V	C V	N V	O V	F V				
$36R$	C VI	N VI	O VI	F VI					
$49R$	N VII	O VII	F VII						
$64R$	O VIII	F VIII							
$81R$	F IX								

Many of these spectra have actually been produced and identified, at least in part, even as far as O VI. On account of the extremely short wave-lengths of the chief lines of highly-ionised atoms, however, the identification of the stage of ionisation which they represent cannot often be verified by calculation of the constants of the

series to which they belong. Their identity has then been deduced by Millikan and Bowen from the expected positions and separations of the doublets or triplets as predicted by the irregular and regular doublet laws, and there can be no doubt that the identifications are correct.

Investigations of ionised atoms are not only of interest as supporting the general theory of atomic structures. They are of great importance in the interpretation of the spectra of the sun and stars, which give a great range of surface temperatures. In the cooler stars, the lines which appear are chiefly those of neutral atoms or compounds, but at successively higher temperatures these are gradually replaced by lines of ionised or multiply-ionised atoms. For instance, in what are believed to be the hottest stars, lines of O III, C III, and C IV have been identified. The knowledge of these spectra which has been gained from laboratory experiments has led to important deductions with regard to the temperatures and densities in stellar atmospheres, through investigations by Saha and by Fowler (R. H.) and Milne.

Another application to an astrophysical problem of great interest has recently been made by Bowen. Apart from a few lines of hydrogen and helium, the spectra of gaseous nebulæ consist of a small number of more or less conspicuous lines, which for a long time were rather vaguely attributed to an unknown element called "nebulium." The advance of atomic physics, however, made the existence of such an element extremely improbable, and we were driven to the conclusion that the nebular lines must be due to a known element, or elements, under conditions not yet imitated in laboratory experiments. The most likely source seemed to be a highly excited, light element, existing in nebulæ under conditions of extremely low density; so low that in the small quantity of gas available in a laboratory experiment no luminosity could be produced. By combining his results with my own, Bowen has proved that several of the brighter lines are due to singly-ionised oxygen and nitrogen, and doubly-ionised oxygen. The structures of these spectra have been very fully investigated, and although the counterparts of the nebular lines do not appear in the laboratory spectra, their positions can be calculated with great accuracy. It is only necessary to suppose that in the nebulæ combinations of terms take place which have been regarded as "forbidden" by the ordinary selection rules. Taking one example, the normal state of the O III atom is represented by two 1_1, two 2_1, and two 2_2 electrons. This configuration gives rise to ${}^3P_{012}$, ${}^1D_2$, and ${}^1S_0$ terms, of which ${}^3P_0$ is the largest and represents the most stable state of the atom. The last two terms are regarded as

metastable states, so that the electron, having come to occupy a corresponding orbit, after excitation, cannot directly pass from one to the other, or to the ^3P state. The relatively small differences in energy of these terms, it should be recalled, is to be attributed to different arrangements of orientation of orbits and spin within the atom, the size and shape of the orbits being the same for all. On account of the extremely low density in nebulæ, it may be supposed that the atoms have a long enough time to change from $^1S_0$ to $^1D_2$ or from $^1D_2$ to $^3P_{12}$ before they are raised to higher states by collision or by the absorption of radiation from stars. The corresponding differences of wave-number agree precisely with the wave-numbers of three important lines in the spectra of the nebulæ. Similar data and reasoning prove that other nebular lines are due to O II and N II, and the long-standing mystery of the nebular spectrum is at last solved. Nebulium no longer menaces our conceptions as to the structure of the periodic table of the elements.

I am well aware that in this rapid survey I have omitted to mention many matters of importance, but I hope I have been able to convey some idea of the contributions of spectroscopy to atomic theory.

CIV.—*The Action of Cuprous Cyanide on Methyl Iodide.*

By Ernald George Justinian Hartley.

In a previous paper (J., 1916, **109**, 1296) the author showed that silver cyanide and methyl iodide combine to give two compounds, $(AgNC)_2$,MeI and AgNC,MeI, according to the temperature of the reaction.

Similar experiments with methyl iodide and cuprous cyanide (for preparation of the latter, see Bassett and Corbet, J., 1924, **125**, 1667) have been carried out with the following results.

At the boiling point of methyl iodide very little combination takes place. When the mixture is heated at 100° in a sealed tube for several hours, a *substance* is formed which has the composition $(CuNC)_3$,MeI. This is a white, microcrystalline powder which can be dried in the air without decomposition, but is unstable, gradually losing methyl iodide, when placed under reduced pressure. On heating to 100°, the cuprous cyanide is recovered almost unchanged.

When the substance is treated with a solution of potassium cyanide, the cuprous cyanide dissolves as the double salt and the methyl iodide separates in oily drops.

When cuprous cyanide and methyl iodide are heated at 100° in the presence of excess of pure dry acetonitrile, the reaction proceeds

differently and a *compound*, CuNC,MeI, is formed almost quantitatively, which dissolves in the acetonitrile and crystallises from the latter in white needles. After traces of oily matter have been washed out with cold acetone, it can be purified by further crystallisations from acetonitrile. It is very sparingly soluble in all other ordinary organic solvents (Found for material dried at 100°: Cu, 28·0; I, 55·0. CuNC,MeI requires Cu, 27·45; I, 54·8%). When it is heated with a solution of potassium cyanide, methylcarbylamine is given off freely. The same double salt is obtained when cuprous cyanide and methyl iodide are heated to about 135°, but tarry products and cuprous iodide are also formed and the yield of CuNC,MeI is small.

Attempts to determine the molecular weight by the elevation of boiling point of acetonitrile gave very discordant results, but all pointed to a high value corresponding to about 3(CuNC,MeI). The stability of this substance as compared with the silver compounds is therefore probably due to the presence of a tricyanogen complex in the molecule.

On treatment with an aqueous solution of silver sulphate or nitrate, silver iodide, silver, and cupric salts are formed. A quantitative determination of the amount of silver iodide and silver produced showed that the action can be represented by the following equation (disregarding the complexity of the molecule):

$$2CuNC,MeI + 2Ag_2SO_4 = 2AgI + 2Ag + CuSO_4 + Cu(NCMe)_2SO_4.$$

That the last compound is present in the solution, although it has not been isolated, seems probable since the liquid is at first almost odourless, but on evaporation in a vacuum over a dehydrating agent a strong smell of carbylamine develops. When the water has all been driven off, very little of the latter can be found in the crystalline residue, which consists almost entirely of copper sulphate, but still gives off a small quantity of carbylamine when warmed with potassium cyanide solution.

No means of isolating this cupric methylcarbylamine sulphate or the corresponding nitrate has been found.

In connexion with these experiments it was noticed that cuprous cyanide combines with acetonitrile with evolution of heat to form an unstable compound, CuNC,MeCN. The nitrile is gradually given off on exposure to the air. Other insoluble cyanides gave similar compounds, *e.g.*, silver ferrocyanide, silver ferricyanide, silver cobalticyanide, and nickelous cyanide. On the other hand, silver cyanide and zinc cyanide did not combine with the nitrile.

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CV.—*Chloroamines as Halogenating Agents. Iodination by a Chloroamine and an Iodide.*

By Alan Edwin Bradfield, Kennedy Joseph Previté Orton, and Idris Cheer Roberts.

Chlorine, bromine chloride, and iodine chloride are respectively formed by the reaction between hydrogen chloride, hydrogen bromide and hydrogen iodide and a chloroamine, according to the equation $>NCl + HX = >NH + XCl$; and a method of chlorination based on the first of these reactions has already been developed (Orton and King, J., 1911, **99**, 1185; Orton and Bradfield, J., 1927, 986). It is now shown that by utilisation of the third reaction (Chattaway, J., 1905, **87**, 145; Orton and W. J. Jones, P., 1909, **25**, 306) the preparation of an acetic acid solution of iodine chloride, which has long been in use as an iodinating agent, is very greatly facilitated, and a method of iodination involving the reaction between dichloramine-T and hydrogen iodide, or, better, sodium iodide, has been applied in the first instance to the preparation of typical iodoanilines, some of them not hitherto described.

Experimental.

Preparation and Use of the Iodinating Reagent.—The reagent may be prepared by slowly adding to an acetic acid solution of dichloramine-T the calculated amount of hydrogen iodide, also dissolved in acetic acid. The first action of hydrogen iodide liberates iodine: $>NCl + 2HI \longrightarrow >NH + HCl + I_2$. The hydrogen chloride formed reacts with another molecule of the chloroamine, liberating chlorine, which combines with the iodine to give a solution with the characteristic orange-yellow colour of iodine chloride. An alternative procedure is to add the calculated quantity of hydrogen chloride to an acetic acid solution of dichloramine-T, containing in solution and suspension the required amount of iodine. It was hoped that by employing a small quantity of hydrogen chloride, a constant low concentration of iodine chloride could be maintained (compare Orton and King, Orton and Bradfield, *locc. cit.*), the acid being re-formed in the substitution by iodine chloride. However, chlorine is produced in the system and even in the presence of considerable excess of iodine, some chlorination occurred.

Finally, it was found most satisfactory to employ the iodide, not as hydrogen iodide, but as the finely powdered sodium salt, which is added in small amounts, with shaking, to a solution of dichloramine-T in glacial acetic acid, little or no liberation of iodine occurring. It should be noted that the reduction in acidity consequ

upon the presence of sodium or potassium ions affects favourably the rate of iodination of anilines.

The general method of employment of the solution of iodine chloride, prepared as above, is to add it slowly to a solution of the aniline in acetic acid. With the simpler anilines, the calculated quantity of the reagent is used, and the reaction proceeds at the ordinary temperature. With substituted anilines, an excess of the reagent and a water-bath temperature are frequently advantageous. The iodo-compound is precipitated by dilution.

The Action of the Reagent on Aniline, 2 : 4-*Dichloroaniline and* 2-*Chloro*-4-*bromoaniline*.—Aniline, with one equivalent of the reagent yields *p*-iodoaniline, with three equivalents, tri-iodoaniline. 2 : 4-Dichloro-6-iodoaniline (Körner and Contardi, *Atti R. Accad. Lincei*, 1913, **22**, 823; Dains, Vaughan, and Janney, *J. Amer. Chem. Soc.*, 1918, **40**, 930), obtained from 2 : 4-dichloroaniline and two equivalents of the reagent, forms an *acetyl* derivative,* thick needles, m. p. 198—199° (Found : X,† 59·7. $C_8H_6ONCl_2I$ requires X, 60·0%). In a similar way, 2-chloro-4-bromoaniline yields 2-*chloro*-4-*bromo*-6-*iodoaniline* as colourless needles, m. p. 95—96° (Found : X, 74·0. $C_6H_4NClBrI$ requires X, 72·9%). The *acetyl* derivative forms colourless needles, m. p. 213° (Found : X, 64·8. $C_8H_6ONClBrI$ requires X, 64·8%). No iodination of 2 : 4-dichloroaniline could be detected after 60 hours' heating at 100° with iodine, in the presence or absence of sodium acetate.

Action of the Reagent on Acetanilide.—On heating acetanilide for 15 minutes with two equivalents of the reagent, *p*-iodoacetanilide is produced (yield, 80%). Prolonged heating gives a poor yield of di-iodo-derivative. The bromination of *p*-iodoacetanilide with double the calculated quantity of bromine, in 70% acetic acid, for 20 minutes at 70°, yields 2-*bromo*-4-*iodoacetanilide* as rhombs, m. p. 143° (Found : X, 61·6. C_8H_7ONBrI requires X, 60·9%). Hydrolysis with 10% aqueous-alcoholic hydrochloric acid, or 10% alcoholic sodium hydroxide, gives 2-*bromo*-4-*iodoaniline*, which crystallises as thick needles, m. p. 75—76° (Found : X, 69·5. C_6H_5NBrI requires X, 69·5%). Slight displacement of the iodine occurs during hydrolysis.

2-*Chloro*-6-*bromo*-4-*iodoaniline* is prepared by chlorination of the above aniline with dichloramine-T and hydrochloric acid. It crystallises from alcohol in fine white needles, m. p. 113—114° (Found : X, 71·6. $C_6H_4NClBrI$ requires X, 72·9%). The *acetyl*

* Prepared by the method of Smith and Orton (J., 1908, **93**, 1249), which has proved successful with all the *s*-trisubstituted anilines described in this paper.

† In all the analyses given in this paper, X denotes mixed halogens.

derivative crystallises from alcohol in fine white needles, m. p. 221° (Found: X, 65·1. $C_8H_6ONClBrI$ requires X, 64·8%). The third s-chlorobromoiodoaniline, isomeric with the two described in the foregoing, was prepared by Körner and Contardi (*loc. cit.*).

Action of the Reagent on o-*Nitroaniline*.—An 80% yield of 4-iodo-2-nitroaniline, m. p. 122°, is obtained by heating *o*-nitroaniline with 1½ equivalents (50% excess) of the reagent for 20—30 minutes. Further heating with an additional quantity of the reagent yields the 4 : 6-di-iodo-derivative (compare Brenans, *Compt. rend.*, 1902, **135**, 177; *Bull. Soc. chim.*, 1902, **27**, 963). Chlorination of 4-iodo-2-nitroaniline with dichloramine-T and hydrochloric acid gives 2-*chloro*-4-*iodo*-6-*nitroaniline* as orange needles, m. p. 124° (Found: X, 54·7. $C_6H_4O_2N_2ClI$ requires X, 54·4%); the *acetyl* derivative forms straw-coloured needles, m. p. 227° (Found: X, 48·2. $C_8H_6O_3N_2ClI$ requires X, 47·7%): and bromination in acetic acid in the cold gives 2-*bromo*-4-*iodo*-6-*nitroaniline* as orange needles, m. p. 117—118° (Found: X, 60·7. $C_6H_4O_2N_2BrI$ requires X, 60·4%), the *acetyl* derivative of which forms straw-coloured needles, m. p. 222° (Found: X, 54·0. $C_8H_6O_3N_2BrI$ requires X, 53·8%).

Action of the Reagent on 4-*Chloro*-2-*nitro- and* 4-*Bromo*-2-*nitro-anilines*.—One equivalent (4 g.) of 4-chloro-2-nitroaniline, prepared by chlorinating *o*-nitroaniline by the usual chloroamine method, was heated for 3 hours on the water-bath with 2 equivalents of the reagent. On cooling, 0·85 g. of orange needles separated, m. p. 136—137°. Gradual dilution gave 1·6 g., m. p. 127°, and 1·2 g., m. p. 80—90°, this impure product being purified through the *acetyl* derivative described below. 4-*Chloro*-2-*iodo*-6-*nitroaniline* forms orange needles, m. p. 137—138° (Found: X, 54·2. $C_6H_4O_2N_2ClI$ requires X, 54·4%), diazotisation of which with amyl nitrite in alcoholic solution yielded 3-chloro-5-iodo-1-nitrobenzene, m. p. 70° (Körner and Contardi, *loc. cit.*). 4-*Chloro*-2-*iodo*-6-*nitroacetanilide* crystallises from alcohol in very pale straw-coloured needles, m. p. 207° (Found: X, 47·1. $C_8H_6O_3N_2ClI$ requires X, 47·7%).

The iodination in a similar manner of 4-bromo-2-nitroaniline, obtained by bromination of *o*-nitroaniline in acetic acid, in the presence of sodium acetate, gave 4-*bromo*-2-*iodo*-6-*nitroaniline* as orange needles, m. p. 146—147° (Found: X, 59·8. $C_6H_4O_2N_2BrI$ requires X, 60·4%). The *acetyl* derivative forms pale yellow needles, m. p. 215° (Found: X, 54·0. $C_8H_6O_3N_2BrI$ requires X, 53·8%). Diazotisation of the aniline in ethyl alcohol with amyl nitrite gave 3-bromo-5-iodo-1-nitrobenzene, m. p. 97° (Körner and Contardi, *loc. cit.*).

The description of the above anilines completes the list of s-tri-

substituted anilines in which one of the positions 2 : 4 : 6 is occupied by the nitro-group and the other two are filled by chlorine, bromine, or iodine atoms.

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BANGOR. [*Received, February 11th*, 1928.]

CVI.—*On the Chemical Individuality of Humulene.*

By A. CHASTON CHAPMAN.

IN the course of a study of the constituents of the essential oil of hops I discovered that this oil contained a considerable proportion (usually from one-third to one-half) of a sesquiterpene, to which I gave the name *humulene*. The properties of this hydrocarbon and of a number of its derivatives were described (J., 1895, **67**, 54, 780). Struck chiefly by the fact that Wallach had shortly before this obtained from caryophyllene a nitrosochloride melting at very nearly the same temperature as humulene nitrosochloride, I examined the new sesquiterpene very closely in order to ascertain whether it might not be an inactive form of caryophyllene. For reasons which seemed to me adequate I came very definitely to the conclusion that these two sesquiterpenes were not identical. Three years later Kremer, Schreiner, and James prepared a number of caryophyllene and humulene derivatives, and as a result of a careful comparison of these arrived at the same conclusion (*Pharm. Arch.*, 1898, **1**, 209). So far as I am aware, no further work on this subject was carried out until 1911, when a paper by Deussen appeared (*J. pr. Chem.*, 1911, **83**, 483) in which he stated that he had identified humulene with "inactive α-caryophyllene."

In 1907, Deussen and Lewinsohn (*Annalen*, **356**, 1), in continuation of some work by Kremer and Schreiner (*Pharm. Arch.*, 1899, **2**, 273), had devoted their attention to a study of certain caryophyllene derivatives, and found that by a process of crystallisation some of these could be resolved into isomeric substances which they designated by the prefixes α- and β-, respectively.

The same authors (*ibid.*, 1908, **359**, 245) also stated that caryophyllene on repeated distillation under reduced pressure yields two lævorotatory hydrocarbons, one having b. p. 132—134°/16 mm., $d^{20°}$ 0·90346, and $[\alpha]_D^{20°}$ − 4·67°, and the other b. p. 128—128·5°/17 mm., $d^{17°}$ 0·91034, and $[\alpha]_D^{17°}$ − 23·57°. The hydrocarbon of lower boiling point yielded 20·8% of a nitrosochloride and over 8% of blue nitrosite, whereas the higher-boiling hydrocarbon yielded little more than traces of a nitrosochloride or of a nitrosite. They concluded that caryophyllene as usually known is a mixture of

inactive caryophyllene with a considerable amount of a lævorotatory hydrocarbon.

In that paper the expression " inactive caryophyllene " appears to have been used for the first time, but in support of the existence of such a hydrocarbon no proof is given. In a subsequent paper, Deussen (*ibid.*, 1909, **369**, 41) assigned a structural formula to the so-called β-caryophyllene, and in collaboration with Loesche and Klemm described a number of derivatives obtained from three hydrocarbons, referred to as α-, β-, and *iso*-caryophyllene respectively, although what the relationship between these was is not very clear. Deussen also states (*loc. cit.*, 1911) that it is the " inactive " caryophyllene with which humulene was considered to be identical, that is to say, the caryophyllene fraction boiling at the higher temperature, and this statement appears to have been accepted by many chemists and to have passed into the literature. In that paper Deussen directed attention to the resemblance between the properties of humulene as described by me, and confirmed by other observers, and those of the higher, or α-caryophyllene fraction, but he gave very little information in regard to the physical constants of the so-called " α-caryophyllene "; he again referred to it as being inactive, and again without adducing any evidence of its actual existence. Certain of the better known derivatives of this hydrocarbon were compared with those of humulene, but the results were of an indefinite character and certainly were not such as to justify the statement that these two hydrocarbons were identical. In this connexion it may be pointed out that whereas humulene yields a nitrosite with great readiness, no such compound could apparently be prepared from the higher caryophyllene fraction, and no attempt appears to have been made to prepare the very characteristic caryophyllene alcohol.

In the following year Deussen (*Annalen*, 1912, **388**, 136) claimed to have devised a method by which β-caryophyllene could be estimated, and by the application of this method reached the conclusion that the hydrocarbon from hop oil which I had described as humulene contained 4% of β-caryophyllene.

In 1914 Deussen in collaboration with Vielitz and Mayer instanced a case in which two quite different halogen derivatives of α-caryophyllene having the same melting point, gave no depression when mixed, whereas this property was in the 1911 paper relied upon as establishing the identity of humulene and the so-called α-caryophyllene, and in 1923 Deussen (*Z. angew. Chem.*, **36**, 348) recapitulated some of the results obtained in the comparison of certain compounds of humulene with those of α-caryophyllene.

EXPERIMENTAL.

Inasmuch as Deussen and his colleagues have assigned the expression α- or inactive caryophyllene to that portion of the crude sesquiterpenes boiling at the higher temperature and having the lower lævorotation, I thought it would be desirable in the first place to repeat their experiments. Five lb. of crude caryophyllene, representing a batch of 40 lb. prepared by the British Drug Houses from clove oil, were submitted to fractional distillation under a pressure of about 3 mm. from a long-necked flask with bulbs. Boiling commenced at 50°, the temperature rose rapidly to 90°, at which the hydrocarbon began to distil in quantity, and then slowly to 105°. Between 105° and 125°—at which point the distillation was stopped—the amount distilling was very small. The densities ($d_{20°}^{20°}$) of the various fractions rose gradually from 0·9024 to 0·9047, and the optical rotations ($\alpha_D^{20°}$; $l = 1$) increased more or less uniformly from $-$ 7·3° to $-$ 9·3°. The final small fraction referred to above (105—125°) had d 0·9138 and α $-$ 11·6°.

As the result of further fractional distillation the caryophyllene was obtained in two main fractions: (1) b. p. 95—97°/3 mm., $d_{20°}^{20°}$ 0·9028, $n_D^{20°}$ 1·4987, $[\alpha]_D$ $-$ 8·2°; (2) b. p. 98—102°/3 mm., $d_{20°}^{20°}$ 0·9035, $n_D^{20°}$ 1·4990, $[\alpha]_D$ $-$ 9·3°.

Continued fractionation failed to effect any further separation and it became clear, therefore, that even when working on large quantities of the crude hydrocarbon, fractional distillation could not be relied upon to effect any further separation than is indicated by the above results. This, it will be seen, is very different from the experience of Deussen and his colleagues, who stated that there had been a separation into two forms of caryophyllene, that one of these, namely, that corresponding with the higher boiling range, was nearly inactive, and consisted mainly of the so-called α-caryophyllene, and further that this was identical with humulene.

The experiments recorded above show, on the contrary, that with rising boiling point the lævorotation showed a small but steady increase. At no point was any fraction obtained which was inactive, or which did not show approximately the steady rise referred to.

Fractional distillation having failed to effect any satisfactory separation so far as this could be judged by reference to the physical properties, recourse was had to the preparation of derivatives for purposes of comparison. Fraction No. 2 was used in the preparation of these derivatives as presumably containing the higher proportion of the so-called α-caryophyllene, although there was in reality no material difference between the two fractions. The humulene used was freshly prepared from 1¼ lb. of fresh hop oil distilled from

green hops, and had the following characteristics: b. p. 99—100°/3 mm., $d_{20^\circ}^{20^\circ}$ 0·8923, $n_D^{20^\circ}$ 1·5001, $[\alpha]_D$ + 1·7°.

Dihydrochloride. Humulene does not appear to form a solid compound with hydrogen chloride, whereas caryophyllene readily forms the crystalline dihydrochloride. When dry hydrogen chloride was passed into the No. 2 caryophyllene fraction an amount of crystalline hydrochloride corresponding with at least 80% of ordinary caryophyllene was obtained. This melted at 69° and had the usual properties of the caryophyllene compound.

Caryophyllene alcohol. A portion of the second fraction, when treated by Bertram and Walbaum's method, gave a large yield of the solid alcohol, which was steam-distilled and purified in the usual way. Humulene, when treated in the same manner, gave no solid product.

Nitrosite. Both the No. 1 and the No. 2 caryophyllene fraction gave substantial yields of the blue nitrosite, which melted, after two recrystallisations from cold dilute acetone, at 115°. The corresponding compound from humulene melted at 114°. The addition of the humulene to the caryophyllene compound depressed the melting point by about 20°.

Nitrosate. Caryophyllene nitrosate was prepared by the usual method and after several recrystallisations melted at 163°. The yield was small. The yield of the corresponding compound from humulene was very much larger, but the melting point was the same, and there was no depression when this was mixed with the compound obtained from crude caryophyllene.

Nitrosochloride. The caryophyllene fraction gave a very small yield of the nitrosochloride as compared with humulene from hop oil, the latter giving at least eight times as much. The melting point in each case after recrystallisation was 176° and no depression was observed when a mixed melting-point determination was made. The conditions adopted for the preparation of the nitrosochloride were those under which the β-caryophyllene compound is not obtained in crystal form.

Nitrolbenzylamine. This compound, when prepared from the nitrosochloride, was found after a second recrystallisation to melt at 136°, which is the same temperature as that at which the humulene derivative melted. A mixture of the crystals showed no depression of melting point.

Nitrolpiperidide. This compound also was prepared from the nitrosochloride and after several recrystallisations melted at 153°. The corresponding humulene compound also melts at this temperature and a mixed melting point showed no depression.

The above results appear to show that the crude sesquiterpene

obtained from clove oil consists substantially of caryophyllene with a rotation of about $[\alpha]_D - 8°$, and that this crude hydrocarbon contains a small proportion—say 5—10%—of humulene.

Working on a very large quantity of crude caryophyllene, I have in fact been unable to obtain an inactive form of this hydrocarbon,* and it is obvious that the hydrocarbon to which Deussen refers as the *α- or inactive caryophyllene* is *neither* more *nor* less than humulene. Probably crude caryophyllene is subject to slight variations depending on the source from which it has been obtained, and other sesquiterpenes than humulene may at times be present.

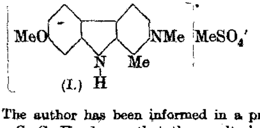
I have to offer my best thanks to Messrs. The British Drug Houses, Ltd., for having placed at my disposal a large quantity of crude caryophyllene, and to Messrs. White, Tomkins, and Courage, Ltd., for the higher fractions of some freshly distilled hop oil from which a new specimen of humulene was prepared. I have also great pleasure in acknowledging the valuable assistance rendered to me by Mr. Gerald Bishop, M.Sc., A.I.C.

CHEMICAL LABORATORIES,
8, DUKE STREET, E.C. 3. [*Received, February 11th*, 1928.]

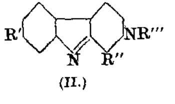
CVII.—*Syntheses in the Indole Series. Part III. The Theory of Anhydronium Base Formation and the Constitution of Methosulphates, with some Observations on the Fluorescence of 5 : 6-Benz-4-carboline and its Derivatives.*

By WILLIAM OGILVY KERMACK and ROBERT HENRY SLATER.

IN support of the view that the anhydronium base formed from harmine methosulphate (I) by the action of alkali has the constitution II (R′ = OMe; R″ = Me; R‴ = Me) and is a derivative of 4-ψ-carboline (II : R′ = R″ = R‴ = H), it has been shown by



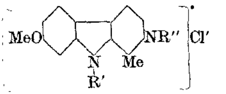
(I.)

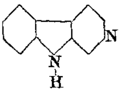


(II.)

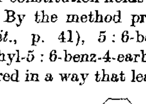
* The author has been informed in a private communication from Professor G. G. Henderson that the results he has obtained in the fractional distillation of large quantities of caryophyllene are very similar indeed to those recorded in this paper. The two main fractions into which he separated caryophyllene both yielded the dihydrochloride and the alcohol.

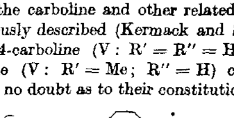
Kermack, Perkin, and Robinson (*J.*, 1922, **121**, 1877) that the propochloride of methylharmine (III : R′ = Pr; R″ = Me) is not identical with the methochloride of propylharmine (III : R′ = Me; R″ = Pr). This evidence is not quite conclusive, inasmuch as it is conceivable that the addition of the alkyl salt to the anhydronium base might take place in such a way that the alkyl group did not attach itself to either nitrogen atom. This possibility, although rather unlikely, must be considered and therefore direct evidence as to the constitution of the anhydronium bases in the carboline series appears desirable. Definite evidence upon this point would obviously be of importance with reference to the general problem of the structure of heterocyclic polynuclear bases.

(III.) 

 (IV.)

Closely related to 4-carboline (IV), of which harmine and all the above compounds are derivatives, is the somewhat more complex 5 : 6-benz-4-carboline (V : R′ = R″ = H). The syntheses of this compound and of some of its derivatives have been described (Kermack and Slater, this vol., p. 32), and it is the comparative ease with which members of the benzcarboline series can be prepared that makes them particularly suitable for the further investigation of the theory of anhydronium base formation. They are compounds very similar to 4-carboline in their properties, and so there seems little doubt that a rigorous proof of the constitution of the anhydronium bases and their metho-salts in this series would imply that a similar constitution holds in the carboline and other related series also. By the method previously described (Kermack and Slater, *loc. cit.*, p. 41), 5 : 6-benz-4-carboline (V : R′ = R″ = H) and 1-methyl-5 : 6-benz-4-carboline (V : R′ = Me; R″ = H) can be prepared in a way that leaves no doubt as to their constitution.

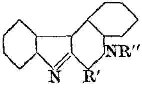
(V.) 

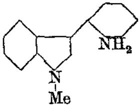
 (VI.)

Now according to the above theory the anhydronium base formed from 5 : 6-benz-4-carboline methosulphate (VI : R′ = R″ = H; R‴ = Me) should be a derivative of 4-ψ-carboline (II : R′ = R″ = R‴ = H) and should possess the constitution VII (R′ = H; R″ =

Me), and so the methosulphate of this anhydronium base ought to be identical with 1-methyl-5 : 6-benz-4-carboline methosulphate, which must have the constitution VI (R′ = R‴ = Me ; R″ = H). This is so, as is shown below, and the identity of these two methosulphates, prepared quite independently, proves definitely that methyl sulphate adds itself on to the pyrrole nitrogen atom of the anhydronium base, and that the theory described above is correct.

(VII.)





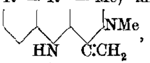
(VIII.)

When heated in benzene suspension with methyl sulphate, 5 : 6-benz-4-carboline yields a bright yellow *methosulphate* (VI : R′ = R″ = H ; R‴ = Me), m. p. 235°, from an aqueous solution of which sodium or ammonium hydroxide readily precipitates an orange *anhydronium base* (VII : R′ = H ; R″ = Me), m. p. 205°. When dissolved in benzene and treated with methyl sulphate, this base gives a *methosulphate* (VI : R′ = R‴ = Me ; R″ = H), m. p. 300°.

1-*Methyl*-5 : 6-*benz*-4-*carboline* (V : R′ = Me ; R″ = H), m. p. 142°, prepared from the formyl derivative of 3-*o*-aminophenyl-1-methylindole (VIII) (Kermack and Slater, *loc. cit.*, p. 44) by the phosphoryl chloride method, is converted by methyl sulphate in benzene solution into a compound, m. p. 300°, which is identical with the methosulphate (VI : R′ = R‴ = Me ; R″ = H) of the anhydronium base described above. This anhydronium base and its methosulphate are therefore properly named 4-*methyl*-5 : 6-*benz*-4-ψ-*carboline* and 1 : 4-*dimethyl*-5 : 6-*benz*-4-*carbolinium methyl sulphate* respectively.

In order to confirm the conclusions just discussed, the work was repeated with 3-methyl-5 : 6-benz-4-carboline (V : R′ = H ; R″ = Me) and 1 : 3-dimethyl-5 : 6-benz-4-carboline (V : R′ = R″ = Me) (Kermack and Slater, *loc. cit.*, pp. 42, 45). 3-*Methyl*-5 : 6-*benz*-4-*carboline methosulphate* (VI : R′ = H ; R″ = R‴ = Me), m. p. 270°, prepared in the usual way, was converted into 3 : 4-*dimethyl*-5 : 6-*benz*-4-ψ-*carboline* (VII : R′ = R″ = Me), m. p. 225°, and this anhydronium base reacted readily with methyl sulphate to form 1 : 3 : 4-*trimethyl*-5 : 6-*benz*-4-*carbolinium methyl sulphate* (VI : R′ = R″ = R‴ = Me), m. p. 292°, which was identical with the methosulphate obtained from 1 : 3-dimethyl-5 : 6-benz-4-carboline. The methyl sulphate and the benzene used in the preparation of these methosulphates must be perfectly dry and neutral to litmus ; in the

earlier experiments, in which this precaution was not taken, the product obtained from 1 : 3-dimethyl-5 : 6-benz-4-carboline melted at 296° and proved to be essentially 1 : 3-*dimethyl*-5 : 6-*benz*-4-*carbolinium methyl sulphate* (VI : R′ = R″ = Me ; R‴ = H) (which could not readily be distinguished by analysis from 1 : 3 : 4-trimethyl-5 : 6-benz-4-carbolinium methyl sulphate), its formation being apparently due to water or methyl hydrogen sulphate in the methyl sulphate used. Before the nature of this product had been ascertained, the possibility (which was considered improbable) suggested itself that the anhydronium base (VII : R′ = R″ = Me) might have reacted in the ethylenic form,



, with methyl sulphate, with the formation of 3-ethyl-5:6-benz-4-carboline methosulphate (VI: R′ = H ; R″ = Et ; R‴ = Me). This possibility was disproved by preparing this *methosulphate* from 3-ethyl-5 : 6-benz-4-carboline (Kermack and Slater, *loc. cit.*, p. 42) ; it melted at 250° and was clearly not identical with the substance of m. p. 292°.

Since the quaternary ammonium base is precipitated from an aqueous solution of 1 : 3 : 4-trimethyl-5 : 6-benz-4-carbolinium methyl sulphate (VI : R′ = R″ = R‴ = Me), both by sodium hydroxide and by ammonium hydroxide, this base appears to be weaker than the quaternary ammonium base of 1 : 4-dimethyl-5 : 6-benz-4-carbolinium methyl sulphate, which is precipitated by sodium hydroxide only (see p. 795). From 4-methylharmine methosulphate, even sodium hydroxide fails to precipitate the quaternary base in the cold (Perkin and Robinson, J., 1919, **115**, 949) ; the present authors have observed, however, that a very large excess of sodium hydroxide does effect precipitation. The extra benzene ring present in the benzcarboline series therefore appears considerably to diminish the basic nature of the nitrogen atom.

As a number of closely related fluorescent compounds were available, they were examined with the object of ascertaining whether any relation exists between the constitution of a compound and the colour of its fluorescence. Solutions of the compounds were prepared by adding 0·1 c.c. of an N/100-solution of the compound in water to 9·8 c.c. of alcohol and 0·1 c.c. of N-hydrochloric acid or of ammonium hydroxide (d 0·880). The acid and the alkaline alcoholic solutions obtained, each containing a compound at a concentration of N/10,000, were arranged by several independent observers according to the colour of their fluorescences, which varied from blue to greenish-yellow. The tubes were illuminated by means

of a carbon arc, which provided a constant source of light and excited a very strong fluorescence. The results are in Table I, 4-methyl-

TABLE I.

Compound.	Acid or alkali added.	Colour of fluorescence.	Highest dilution showing fluorescence.
1 : 3-Dimethyl-5 : 6-benz-4-carboline hydrochloride	NH_4OH	Blue	$N/10^6$
1-Methyl-5 : 6-benz-4-carboline hydrochloride....................	,,	,,	$N/2.10^6$
4-Methylharmine methosulphate	HCl	,,	$N/10^7$
3-Ethyl-5 : 6-benz-4-carboline hydrochloride....................	NH_4OH	,,	$N/4.10^5$
5 : 6-Benz-4-carboline hydrochloride	,,	,,	$N/10^6$
3-Methyl-5 : 6-benz-4-carboline hydrochloride....................	,,	,,	$N/4.10^5$
4-Methylharmine methosulphate	,,	,,	$N/10^7$
3-Ethyl-5 : 6-benz-4-carboline hydrochloride....................	HCl	Blue with greenish tinge	$N/2.10^7$
3-Methyl-5 : 6-benz-4-carboline *hydrochloride*....................	,,	,, ,,	$N/10^7$
Quinine hydrochloride	,,	,, ,,	$N/10^7$
3 : 4-Dimethyl-5 : 6-benz-4-ψ-carboline hydrochloride	,,	Greenish-blue	$N/2.10^7$
3-Methyl-5 : 6-benz-4-carboline methosulphate	,,	,,	$N/2.10^7$
3-Ethyl-5 : 6-benz-4-carboline methosulphate	,,	,,	$N/10^7$
1 : 3-Dimethyl-5 : 6-benz-4-carboline hydrochloride	,,	Bluish-green	$N/2.10^7$
5 : 6-Benz-4-carboline hydrochloride	,,	,,	$N/10^7$
3 : 4-Dimethyl-5 : 6-benz-4-ψ-carboline hydrochloride	NH_4OH	Green	$N/10^7$
3-Methyl-5 : 6-benz-4-carboline methosulphate	,,	,,	$N/10^7$
3-Ethyl-5 : 6-benz-4-carboline *methosulphate*	,,	,,	$N/10^7$
4-Methyl-5 : 6-benz-4-ψ-carboline hydrochloride	HCl	,,	$N/2.10^7$
5 : 6-Benz-4-carboline methosulphate	,,	,,	$N/2.10^7$
1-Methyl-5 : 6-benz-4-carboline hydrochloride....................	,,	,,	$N/10^7$
1 : 3 : 4-Trimethyl-5 : 6-benz-4-carbolinium methyl sulphate	,,	,,	$N/10^7$
4-Methyl-5 : 6-benz-4-ψ-carboline hydrochloride	NH_4OH	Yellowish-green	$N/4.10^6$
5 : 6-Benz-4-carboline methosulphate	,,	,,	$N/4.10^6$
1 : 3 : 4-Trimethyl-5 : 6-benz-4-carbolinium methyl sulphate	,,	,,	$N/4.10^6$
1 : 4-Dimethyl-5 : 6-benz-4-carbolinium methyl sulphate	,,	Greenish-yellow	$N/10^7$
1 : 4-Dimethyl-5 : 6-benz-4-carbolinium methyl sulphate	HCl	,,	$N/10^7$
Quinine hydrochloride	NH_4OH	None at $N/10^4$	Less than $N/10^4$

harmine methosulphate and quinine hydrochloride being included for comparison. *N*/10,000-Solutions of these compounds in water and in *N*/100-hydrochloric acid were also examined: the order for these was the same as that for the hydrochloric acid–alcohol solutions. Addition of alkali to the aqueous solutions precipitated the bases in many cases and so destroyed the fluorescence. Alcoholic solutions containing sodium hydroxide (0·1 c.c. of *N*/100-carboline solution, 9·7 c.c. of alcohol, 0·2 c.c. of 5*N*-sodium hydroxide) exhibited fluorescences identical with those of solutions containing ammonium hydroxide.

The chief deductions to be drawn from the table are as follows. A methyl (or ethyl) group attached to the carbon atom in position 3 (see formula V) invariably renders the fluorescence more blue. With the introduction of a methyl group attached to either nitrogen atom, the fluorescence in acid solution becomes more yellow, the effect being greater when the methyl group is in position 1 than when it is in position 4. In acid solution the effect of a methyl group in position 3 is almost balanced by that of a methyl group in position 4. In alkaline solution a methyl group in position 1 renders the fluorescence more blue, whereas in position 4 it makes the fluorescence more green. In alkaline solution a methyl group in the 4-position is much more powerful in making the fluorescence more green than one in the 3-position is in making it blue. 1-Methyl-5 : 6-benz-4-carboline fluoresces bluer in alkaline solution than in acid solution, whereas 4-methyl-5 : 6-benz-4-ψ-carboline fluoresces yellower in alkaline solution than in acid solution. It seems a probable assumption that the yellowish-green colour of 4-methyl-5 : 6-benz-4-ψ-carboline in alkaline solution is due to the existence of the ψ-carboline structure.

The compounds which contain a methyl group in the 4-position (that is, those compounds whose bases cannot possess a normal structure in alkaline solution) fluoresce more yellow in alkaline than in acid solution, whereas those compounds not possessing a methyl group in this position are bluer in alkaline than in acid solution. Hence derivatives of the normal base (5 : 6-benz-4-carboline) fluoresce very blue, particularly in alkaline solution, and 5 : 6-benz-4-carboline and 3-methyl-5 : 6-benz-4-carboline exist essentially in the normal form.

The figures in the fourth column in Table I represent the concentrations at which the fluorescences are just visible. They are only approximate, but it is clear that the fluorescence of these compounds is usually considerably stronger in acid than in alkaline solution. In respect to colour and intensity of fluorescence, pairs of compounds such as 5 : 6-benz-4-carboline methosulphate and 4-methyl-5 : 6-

benz-4-ψ-carboline hydrochloride, which contain the same organic kation, are identical.

Experimental.

5 : 6-*Benz-4-carboline Methosulphate* (VI : R′ = R″ = H ; R‴ = Me).—The method here described is of general application for the preparation of 5 : 6-benz-4-carboline methosulphates. They are best recrystallised from methyl alcohol. The absence of by-product such as VI (R′ = R″ = Me ; R‴ = H) is readily indicated by the *non*-production of a precipitate when a few drops of concentrated hydrochloric acid are added to an aqueous solution of the methosulphate.

Finely powdered 5 : 6-benz-4-carboline (3 g.), dry benzene (10 c.c.), and methyl sulphate (2·5 g.) were heated together on the steam-bath for 30 minutes. The product that separated was recrystallised from a small quantity of boiling methyl alcohol, 5 : 6-*benz-4-carboline methosulphate* being obtained in thick, bright yellow, prismatic needles which exhibited a greenish fluorescence, m. p. 235° (Found : C, 58·3 ; H, 5·3. $2C_{17}H_{16}O_4N_2S,CH_3{\cdot}OH$ requires C, 58·1 ; H, 5·0%). The salt is readily soluble in water and in methyl and ethyl alcohol, the solutions exhibiting a green fluorescence. Its solution in concentrated sulphuric acid also exhibits a green fluorescence, which changes to deep greenish-blue on warming.

4-*Methyl*-5 : 6-*benz-4-ψ-carboline* (VII : R′ = H ; R″ = Me) was obtained in a hydrated form as an orange precipitate when an aqueous solution of 5 : 6-benz-4-carboline methosulphate was treated with an excess of ammonium hydroxide in the cold (it is also precipitated by sodium hydroxide). It crystallised from boiling water, in which it was only sparingly soluble, in fine, orange, prismatic needles which, after being heated at 100° for 6 hours, darkened at 190° and melted at 205° (Found : C, 82·6 ; H, 5·2. $C_{16}H_{12}N_2$ requires C, 82·8 ; H, 5·2%). It is readily soluble in alcohol and moderately easily soluble in benzene, the solutions exhibiting a brilliant green fluorescence.

1 : 4-*Dimethyl*-5 : 6-*benz-4-carbolinium methyl sulphate* (VI : R′ = R‴ = Me ; R″ = H), prepared both from 4-methyl-5 : 6-benz-4-ψ-carboline and from 1-methyl-5 : 6-benz-4-carboline, forms long, chrome-yellow, rectangular prismatic needles which exhibit a greenish fluorescence ; m. p. 300° (Found : C, 59·8 ; H, 5·2. $C_{18}H_{18}O_4N_2S$ requires C, 60·3 ; H, 5·0%). Its solutions in water, boiling methyl alcohol, and concentrated sulphuric acid exhibit a greenish-yellow fluorescence, the last becoming greenish-blue on warming. The addition of sodium hydroxide, but not ammonium hydroxide, to the aqueous solution precipitates the hydrated

quaternary ammonium hydroxide as a voluminous, buff, amorphous compound.

1-*Methyl*-5 : 6-*benz*-4-*carboline* (V : R′ = Me ; R″ = H).—This was prepared from 3-*o*-aminophenyl-1-methylindole (5 g.) by a method almost exactly identical with that described for the preparation of 5 : 6-benz-4-carboline (Kermack and Slater, *loc. cit.*, p. 41), the only differences being the extraction of the crude formyl derivative with ether, its drying over anhydrous sodium sulphate, and the use of 30 c.c. of toluene and 12 c.c. of phosphoryl chloride. The *benzcarboline* crystallised from ligroin, containing a little solid potassium hydroxide, in long, pale pink, feathery needles exhibiting radial formation; m. p. 142° (Found: C, 83·3; H, 5·4. $C_{16}H_{12}N_2$ requires C, 82·8; H, 5·2%). It is readily soluble in alcohol, benzene, and chloroform, but much less soluble in ligroin and light petroleum; these solutions exhibit a brilliant green fluorescence. The hydrochloride is only sparingly soluble in water and gives none of the usual indole reactions.

3-*Methyl*-5 : 6-*benz*-4-*carboline methosulphate* (VI : R′ = H ; R″ = R‴ = Me) forms stout, bright yellow, prismatic needles, m. p. 270° (Found: C, 60·4; H, 5·2; N, 7·9. $C_{18}H_{18}O_4N_2S$ requires C, 60·3; H, 5·0; N, 7·8%). Its solutions in water, boiling methyl alcohol, and concentrated sulphuric acid exhibit a vivid greenish-blue fluorescence, the last becoming brilliant blue on warming and bluish-green on dilution.

3 : 4-*Dimethyl*-5 : 6-*benz*-4-ψ-*carboline* (VII : R′ = R″ = Me).—To an aqueous solution of 3-methyl-5 : 6-benz-4-carboline methosulphate, ammonium hydroxide was added until precipitation of the hydrated quaternary ammonium hydroxide was complete. (This is also precipitated by sodium hydroxide.) The *base* crystallised from boiling water in long, yellow, felted needles which, after being heated for 6 hours at 100°, darkened slightly at 200° and melted at 225° (Found: C, 82·6; H, 5·8; N, 11·2. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7; N, 11·4%). It is readily soluble in alcohol and benzene, the solutions exhibiting a brilliant greenish-blue fluorescence.

1 : 3 : 4-*Trimethyl*-5 : 6-*benz*-4-*carbolinium methyl sulphate* (VI : R′ = R″ = R‴ = Me), prepared both from 3 : 4-dimethyl-5 : 6-benz-4-ψ-carboline and from 1 : 3-dimethyl-5 : 6-benz-4-carboline, forms long, chrome-yellow, rectangular prismatic needles which exhibit a bright green fluorescence; m. p. 292° (Found: C, 61·2; H, 5·4; N, 7·3. $C_{19}H_{20}O_4N_2S$ requires C, 61·3; H, 5·4; N, 7·5%). Its solutions in water, hot methyl alcohol, and concentrated sulphuric acid exhibit a vivid green fluorescence, the last becoming brilliant blue on warming and greenish-blue on dilution. The addition of sodium hydroxide or ammonium hydroxide to the

aqueous solution precipitates the quaternary ammonium hydroxide as a fine emulsion, from which yellow crystals slowly separate.

3-Ethyl-5 : 6-benz-4-carboline methosulphate (VI : R′ = H ; R″ = Et ; R‴ = Me) forms pale yellow, tetragonal plates, m. p. 250° (Found : C, 61·6 ; H, 5·6. $C_{19}H_{20}O_4N_2S$ requires C, 61·3 ; H, 5·4%). Its solutions in water, boiling methyl alcohol, and concentrated sulphuric acid exhibit a greenish-blue fluorescence, the last becoming brilliant blue on warming. The addition of sodium hydroxide or ammonium hydroxide to the aqueous solution gives at once a voluminous, bright yellow, crystalline precipitate of the hydrated quaternary ammonium hydroxide.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research and to the Trustees of the Carnegie Trust for the Universities of Scotland, for a personal payment and a Research Fellowship, respectively, to one of them (R. H. S.), and to the Government Grant Committee of the Royal Society for a grant which helped to defray the cost of this investigation. They are also indebted to Mr. F. Hall, Oxford, for the analytical results.

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EDINBURGH. [*Received, December 29th, 1927.*]

CVIII.—*Internal Equilibrium in Liquid Sulphur. Part I.*

By DALZIEL LLEWELLYN HAMMICK, WILFRID R. COUSINS, and EDWARD J. LANGFORD.

THE commonly accepted view as to the nature of liquid sulphur is that it contains, when in internal equilibrium, at least two molecular species, S_λ and S_μ. Attempts to estimate the relative proportions of the two forms present at different temperatures have been made by Alex. Smith and his collaborators (Smith and Holmes, *J. Amer. Chem. Soc.*, 1905, **27**, 979 ; Smith and Carson, *Z. physikal. Chem.*, 1907, **57**, 685), and their results are embodied in the familiar internal-equilibrium curve for liquid sulphur. The data from which their curve (see Fig. 1) was plotted were obtained by heating specimens of sulphur in open tubes until internal equilibrium had been reached at various temperatures between the melting and boiling points of sulphur, the liquid being then poured into ice-water to fix the equilibrium. Specimens chilled from below about 150° solidified rapidly into hard drops ; on the other hand, when higher temperatures were used, the cooled mass was plastic and was kept

for several days until it had hardened sufficiently to be ground. The dried and powdered specimens were then extracted, under standardised conditions, with carbon disulphide in a Soxhlet apparatus, and the amount of insoluble sulphur was estimated. If the amounts of insoluble sulphur thus found be taken as a measure of the amounts of S_μ present in the original specimens of liquid sulphur, an allelotropic line can be plotted.

It is, however, difficult to believe that this allelotropic line really represents the internal equilibrium in liquid sulphur. It is unlike any other such line at present known. Its course implies a large and rapid change in the magnitude of the heat of transformation of S_λ into S_μ between 170° and 200°, at which point the curve becomes practically vertical, the heat of transformation in consequence becoming negligible and the equilibrium composition independent of temperature. Smith and Holmes (*loc. cit.*) were aware of the difficulties in the way of the ordinary physical interpretation of the results, for they say that "caution is necessary *in the interpretation of the data in regard to sulphur supercooled* from very high temperatures," and that "such data should be used only for comparing the effects of variables other than temperature." In short, before we can accept the line, we must be satisfied that the sudden change of direction of the line to the vertical at about 160—170° is not due to the rate of chilling of the sulphur being insufficient to prevent reversion of S_μ to S_λ. The extent to which this reversion occurs will depend on the conditions of experiment, and in particular on (1) the size of the droplets as they fall into the ice-water, and (2) the speed with which they are transferred from the heating apparatus into the ice-water. If, therefore, the vertical part of the so-called allelotropic line is caused by ineffective chilling, a finer division of the liquid sulphur and a method of transference from the heating apparatus to the chilling vessel more rapid than pouring should at least transfer the vertical part of the line towards the S_μ axis.

In order to ensure as fine division of the liquid sulphur as possible we have made fine suspensions of liquid sulphur in a mixture of sulphuric acid and ammonium sulphate of approximately the same density as liquid sulphur. In order to accelerate transference from the heating vessel to the chilling bath, we have constructed an apparatus in which, by knocking a hole in the vessel containing the "emulsified" sulphur, the contents could be dropped straight into ice-water.

EXPERIMENTAL.

The Production of the Sulphur Suspensions.—The apparatus used consisted of a large boiling-tube that fitted into a cylindrical resist-

ance furnace. The boiling-tube contained a mixture of 45 g. of recrystallised ammonium sulphate and 30 c.c. of concentrated sulphuric acid, and was fitted with a thermometer and a "bulb" stirrer at the end of a hollow glass tube mounted on a ball-bearing bicycle hub and driven by an electric motor. Experience showed that good suspensions of liquid sulphur in the molten acid sulphate could be obtained only with "bulb" stirrers, and that even with these the fineness of the suspensions varied considerably for a given speed of rotation.

It was found that the only effect of the acid sulphate on the sulphur was to oxidise it to an extent depending on the temperature. The production of sulphur dioxide was no disadvantage, because, although its anticatalytic effect on the rate of attainment of equilibrium made long heating necessary, its presence tended to prevent reversion on chilling. The sulphur as such was absolutely insoluble in the sulphate mixture. This point was tested by pouring the clear supernatant liquid from the melted sulphur into water, whereupon no sulphur separated.

To carry out an experiment, the semi-solid acid sulphate was heated with a flame until it was fused and its temperature raised a few degrees above that at which it was proposed to conduct a run. The electric heating furnace (which had been started some time previously) was now placed round the boiling-tube. The base of the furnace was closed with a removable asbestos cap, and as much of the top of the tube as possible was plugged with lead foil lined with asbestos to minimise heat loss and oxidation of sulphur. The stirring-motor was started and about 20 g. of powdered sulphur (recrystallised from carbon disulphide or toluene) were added in small quantities at a time over about 10 minutes. The thermometer in the mixture showed that if the furnace was allowed 3—4 hours in which to reach thermal equilibrium before the experiment started, the temperature did not vary by more than 1°. Stirring was rapid, though too fast running of the motor caused the liquid sulphur to stick to the stirrer and the walls of the tube.

Although internal equilibrium was reached in an hour even at the lower temperatures, it was found necessary to keep the sulphur stirred for 4—5 hours, especially at the higher temperatures when it was in the sticky state, before really fine suspensions could be obtained.

Chilling the Suspensions.—Passing through the hollow stirrer was a hard-glass rod which was kept clear of the liquid mixture by a coil-spring between a knob at the top of the rod and the bearing of the stirrer. In order to get the suspension out of the boiling tube, the cap at the base of the furnace was removed and, while

the stirrer was still running, the top of the hard glass rod was struck with a mallet. The end of the rod knocked the bottom out of the tube and the contents fell directly into a large beaker of ice-water, which was kept rapidly stirred. The presence of ice in the water was a disadvantage, as the sulphur droplets tended to coagulate on it.

Analysis of the Chilled Sulphur.—Chillings from temperatures up to 150° readily gave fine droplets of sulphur that hardened rapidly. When obtained from higher temperatures, the droplets were sticky and required anything up to 5 days before they became hard enough to grind. The specimens were first washed in running water for 12 hours and then allowed to dry and harden on a porous plate in a vacuum desiccator. Fragments of broken glass from the boiling-tube were then picked out by hand. The yields, *before analysis*, were divided into two classes: those containing droplets of diameter up to 0·5 mm. were classified as "good," droplets up to 1 mm. in diameter were graded as "fair," and others rejected. When obtained from temperatures up to 160—170°, the size of the droplets made little difference to the content of S_μ; as will be seen, however, the amount of S_μ in samples from the higher temperatures differed considerably according to which grade they belonged to.

When hard, the specimens were ground in a mortar, sieved through a No. 30 mesh, and subjected to a further drying. The amount of insoluble S_μ was then estimated by Smith's method (see below). It was found necessary to extract and dry the extraction thimbles to constant weight before use, and to carry out all weighings as quickly as possible. About 8 g. of chilled sulphur were used in each extraction, which was carried out by allowing the thimble to fill and empty 6 times in 25 minutes. The residual insoluble S_μ was rapidly drained and allowed to dry in a vacuum desiccator to approximately constant weight.

As was found by Smith and Holmes (*Z. physikal. Chem.*, 1903, **42**, 474), so-called insoluble sulphur dissolves very slowly in carbon disulphide. To correct for this, those authors made a series of artificial mixtures of S_λ and S_μ and weighed the amounts of S_μ remaining after extraction; they thus obtained a curve which could be used to correct for loss of S_μ in any particular mixture extracted. Obviously the magnitude of the correction will depend on the particular extractor used, and is not of general application. We have attempted to estimate the effect of S_μ solubility in our experiments by continuing the extraction of specimens of chilled sulphur by a further 6 fillings of the Soxhlet thimble. Thus, in two experiments we found that 2·881 and 2·735 g. of extracted sulphur (*i.e.*,

S_μ) lost 0·086 and 0·091 g. on further extraction. This corresponds to a loss of under 3% on the S_μ present in 8 g. charges of unextracted sulphur. As this is within our experimental error, and having regard to the fact that we were more particularly concerned with temperatures at which the percentage of S_μ was considerable, we have not applied any correction to our results. The effect of a correction would be, of course, to raise the recorded percentages of S_μ found.

The data in Tables I and II refer respectively to those specimens of chilled sulphur droplets graded as "good" and "fair"; T gives the temperature at which the sulphur was allowed to attain internal equilibrium before chilling.

TABLE I.

T	150°	160°	170°	170°	175°	178°	180°	180°	186°	196°	210°
S_μ %	4·5	8·9	18·6	18·1	23·5	23·5	25·0	25·1	29·4	35·1	38·7
S_μ %	4·1	9·2	18·7	18·1	21·9	—	25·0	25·2	28·9	34·8	—
S_μ % (mean)	4·3	9·1	18·4		22·7	23·5	25·0	25·2	28·7	35·0	38·7
T	213°	223°	227°	229°	242°	260°	263°	271°	279°	280°	287°
S_μ %	38·8	37·1	39·0	40·8	39·6	38·6	37·7	39·9	37·9	39·3	39·5
S_μ %	—	37·0	—	40·5	39·6	38·5	—	—	37·9	39·2	40·4
S_μ % (*mean*)	38·8	37·1	39·0	40·7	39·6	38·6	37·7	39·9	37·9	39·3	39·9

TABLE II.

T	240°	245°	254°	260°	261°	266°	271°	271°	290°	299°
S_μ %	33·9	34·4	31·5	33·7	32·6	34·8	32·4	34·6	33·2	31·7
S_μ %	33·8	34·0	30·0	—	—	—	—	—	—	—
S_μ % (mean)	33·9	34·2	30·8	33·7	32·6	34·8	32·4	34·6	33·2	31·7

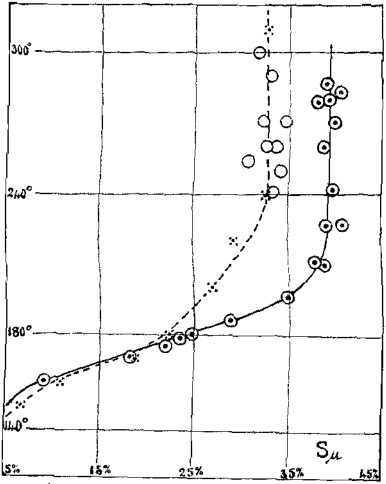
Conclusions.

The effect of our method of chilling liquefied sulphur has been, in the case of our most finely divided specimens (dotted circles ⊙ on diagram), to prolong the transverse portion of Smith and Holmes's allelotropic line and to arrive at an approximately vertical line at about 40% S_μ instead of at about 33%. As was pointed out above, this result is to be taken as implying that the cause of the vertical trend of the curve is to be found in ineffective chilling, a conclusion which is strongly supported by the fact that our less effectively chilled samples gave percentages of insoluble sulphur (plain circles on diagram) that lie on and about Smith and Holmes's curve. It is thus clearly incorrect to regard plots of the kind shown in the diagram as true allelotropic lines giving the relative amounts of S_λ and S_μ in liquid sulphur at different temperatures.

In connexion with the methods used by ourselves and by Smith and his collaborators for estimating the amounts of insoluble sulphur in chilled sulphur, it should be pointed out that we have no inform-

ation as to what is happening to the chilled specimens while they are hardening. *As Smith himself noticed (loc. cit.)*, sulphur in the plastic condition passes through the Soxhlet thimbles; how and why it does so is a matter for further investigation. The fact that quite definite changes in the properties of the sulphur occur during the process of hardening makes it questionable whether the amount

FIG. 1.



Authors ⊙ ⊙ ○. *Smith* :•: :•: :•:.

of insoluble "hard" sulphur at the end of that period is in reality the amount of insoluble S_μ in the freshly chilled plastic mass This point will be discussed in a subsequent communication.

In conclusion, the authors wish to acknowledge a grant from Messrs. Brunner Mond and Co. which has defrayed part of the cost of this investigation.

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CIX.—*The Mechanism of the Degradation of Fatty Acids by Mould Fungi. Part I.*

By THOMAS KENNEDY WALKER and PHILIP DALTON COPPOCK.

IN investigations designed to throw light on the stages by which fatty acid catabolism proceeds in the animal body, endeavours have often been made to confirm the results of physiological studies by the use of chemical reagents *in vitro*. Certain reactions which proceed in the mammalian body are also of normal occurrence in the metabolic processes of fermentative organisms. This suggested the possibility that the latter might be capable of effecting the enzymic degradation of fatty acids by processes identical with or closely similar to those by which it is believed breakdown is occasioned in living animal tissue, and the present communication deals with a study of the fermentation of propionic acid by the mould *Aspergillus niger*. The case of this acid is of particular interest, since physiological experiments hitherto have not indicated definitely the initial stage of its degradation, and Dakin (*J. Biol. Chem.*, 1926, **67**, 341) has pointed out that its direct conversion into lactic acid, if such could be demonstrated, would furnish a unique example of α-oxidation *in vivo* of a normal fatty acid. The experiments of Ringer (*J. Biol. Chem.*, 1912, **12**, 511) suggest indirectly that oxidation to lactic acid does occur, but Blum and Worringer (*Bull. Soc. Chim. biol.*, 1920, **2**, 88) incline to the view that pyruvic acid is the first product, subsequently undergoing asymmetric reduction to *l*-lactic acid, a conclusion which Knoop has questioned (*Z. physiol. Chem.*, 1923, **130**, 388). Raper (*Biochem. J.*, 1914, **8**, 320) has suggested that, by analogy with the manner in which saturated α-methyl fatty acids react with hydrogen peroxide, propionic acid may be attacked at its β-carbon atom, which forms part of a methyl group. If such should be the case, the reaction might be expected to yield, ultimately, malonic semi-aldehyde together, probably, with malonic acid. Dakin (*J. Biol. Chem.*, 1908, **4**, 227) obtained acetaldehyde by the action of hydrogen peroxide on propionic acid; this may have arisen from decarboxylation of the unstable malonic semi-aldehyde, though its formation from lactic acid is equally probable. In a recent paper (*ibid.*, 1926, **67**, 341) the same author has put forward an hypothesis by which propionic acid might undergo in the body dehydrogenation of the αβ-type, yielding acrylic acid which, in turn, might yield hydracrylic or conceivably lactic acid. This view receives support from the fact that succinic acid is oxidised to fumaric acid by muscle tissue and that acrylic acid, like propionic acid, yields glucose in the phloridzinised dog. Dakin was not able,

however, to obtain experimental evidence in support of this hypothesis.

In an investigation undertaken with a different object, Raistrick and Clark (*Biochem. J.*, 1919, **13**, 329) experienced difficulty in inducing *A. niger* to grow in media containing ammonium or sodium propionate as the sole source of carbon. Only in one instance, on sodium propionate, did development occur and a small yield of oxalic acid result. On salts of lactic acid good growth unaccompanied by oxalic acid formation took place, and ammonium pyruvate gave good growth and small yields of oxalic acid. On this and other evidence the authors questioned whether the oxalic acid had not arisen by purely chemical changes during sterilisation of the media rather than by the biological agency of the mould.

The present authors have found that *A. niger* may be cultivated readily on dilute aqueous solutions of calcium propionate together with the requisite inorganic salts. When incubated at 32°, such cultures gave positive thiophen tests for lactic acid (Fletcher and Gowland Hopkins, *J. Physiol.*, 1907, **35**, 247) on or about the ninth day. Thereafter, the thiophen colour reaction became fainter or disappeared, and about the twelfth or thirteenth day pyruvic acid was detected by the coloration given with benzenediazonium chloride in presence of sodium acetate (Bamberger and Müller, *Ber.*, 1894, **27**, 147). That the latter coloration was due actually to pyruvic acid and not to malonic acid or its semi-aldehyde, which also react with the diazonium acetate, was proved in several experiments in none of which was it possible to isolate a formazyl derivative of malonic acid or of its semi-aldehyde by addition of the diazonium salt to the cultures; whereas, in each instance, the simultaneous addition of aminoguanidine nitrate to other samples of the same cultures yielded its condensation product with pyruvic acid (Wedekind and Bronstein, *Annalen*, 1899, **307**, 298).

In these experiments, lactic acid was detected in every case prior to the appearance of pyruvic acid. The presence of lactic acid was confirmed by its conversion by sulphuric acid into acetaldehyde and formic acid, the latter being analysed as the lead salt. These results made it probable that the pyruvic acid had arisen by oxidation o the lactic acid, a biological transformation which has already bee demonstrated in the cases of other fermentative organisms (com pare Mazé, *Compt. rend. Soc. Biol.*, 1918, **81**, 1150; Quastel *Biochem. J.*, 1925, **19**, 304; Kayser, *Bull. Soc. Chim. biol.*, 1924, **6** 345). The mould was therefore cultivated on a calcium lactat medium and was found to yield pyruvic acid, which was detected b benzenediazonium acetate on the tenth day and isolated subse quently in the form of its compound with aminoguanidine (Wed

kind and Bronstein, *loc. cit.*). In another experiment pyruvic acid was produced on the seventh day and was characterised as the *p*-nitrophenylhydrazone.

Nagayama (*Biochem. Z.*, 1921, **116**, 303) has shown that a number of moulds, including *A. niger mutante*, produce acetaldehyde when grown on calcium pyruvate as sole source of carbon. The fact that cultures of *A. niger* on calcium propionate developed a distinct odour of acetaldehyde led us to attempt to isolate the latter from the various culture solutions by carrying out fermentations in the presence of sodium sulphite and of calcium sulphite according to the method of Neuberg and Reinfurth (*Biochem. Z.*, 1918, **89**, 389). The results were entirely negative and in the case of calcium lactate cultures strong reduction occurred accompanied by darkening of the liquid and evolution of hydrogen sulphide. Nevertheless, in pyruvate and lactate cultures the transitory existence of acetaldehyde was indicated by the fact that after 28 days these were found to contain traces of ethyl alcohol, produced presumably either by direct reduction or by dismutation (biologically induced Cannizzaro reaction) of the aldehyde. The alcohol was oxidised to acetaldehyde and characterised as aldomedon (Neuberg and Reinfurth, *Biochem. Z.*, 1920, **106**, 281). By the action of certain yeasts on calcium lactate Kayser (*loc. cit.*) obtained ethyl alcohol, in addition to pyruvic acid. Blank experiments in which sterile solutions of calcium pyruvate and the inorganic salts of the medium were mixed and maintained for several weeks at 32° gave no traces of acetaldehyde or ethyl alcohol. Hence it seems probable that *A. niger* brings about the conversion of pyruvic acid into acetaldehyde by the agency of the enzyme carboxylase. If the ethyl alcohol produced in these fermentations arises by dismutation of acetaldehyde, then acetic acid must be formed simultaneously; and Neuberg (*Biochem. Z.*, 1914, **67**, 90) obtained this acid as the main product of the putrefactive fermentation of pyruvic acid. Its presence in our fermenting media has not yet been proved, but indirect evidence of its occurrence was furnished by the following facts: (*a*) Separate cultures of *A. niger* on the calcium salts of propionic, lactic, and pyruvic acids in the later stages of fermentation gave positive naphtharesorcinol tests for glyoxylic acid in all cases; (*b*) a calcium lactate culture yielded a small amount of calcium oxalate; and (*c*) Challenger, Subramaniam, and the present authors (J., 1927, 200, 3044) had already shown that the fermentation of calcium acetate by *A. niger* follows the course: acetic acid$\longrightarrow$glycollic acid$\longrightarrow$glyoxylic acid$\longrightarrow$ oxalic acid. Hence it is to be inferred that the oxalic acid isolated in the present instance had been produced in this manner. Incidentally, in view of the above, the mycological genesis of the oxalic acid

obtained by Raistrick and Clark (*loc. cit.*) must be regarded as verified.

EXPERIMENTAL.

The *A. niger* strain, and the medium containing the inorganic salts, designated "Solution M," were the same as those employed by Challenger, Subramaniam, and one of us (*loc. cit.*). The usual precautions were observed to ensure aseptic conditions in working and results were checked by blank experiments carried out under identical conditions.

Fermentation of Calcium Propionate. Detection of Lactic and Pyruvic Acids.—Three separate experiments were carried out in which, in each case, calcium propionate (25 g.) in solution M (2500 c.c.) was inoculated by young test-tube cultures of *A. niger* on the same medium, and the mixture incubated at 32°. In these three cases lactic acid was detected qualitatively after 9, 10, and 9 days, and pyruvic acid after 14, 14, and 13 days, respectively. In one of these experiments the thiophen colour test was markedly distinct on the eleventh day, whereupon 1000 c.c. of the medium were removed, filtered, and evaporated to dryness and the residue was distilled with 60 c.c. of 60% sulphuric acid. A strong smell of acetaldehyde, which gave way to that of formic acid, was observed. The distillate was neutralised with caustic soda and evaporated to dryness, and the residue extracted several times with methyl alcohol, which removed sodium propionate and left 0·76 g. of insoluble material, presumably sodium formate. The latter, in 5 c.c. of water, gave with 1·6 g. of lead nitrate in 8 c.c. of water, a white precipitate (1·4 g.), which was washed with cold water, crystallised twice from hot water, and dried over calcium chloride (Found Pb, 69·6. Calc.: Pb, 69·7%).

In another of the experiments in which a positive test for pyruvi acid had been obtained faintly on the thirteenth and very definitel on the fourteenth day, 2000 c.c. of the medium were immediatel filtered and treated with 10 g. of aminoguanidine nitrate and th mixture was strongly cooled. After 48 hours the precipitat (3·4 g.) was removed, washed with cold water, and recrystallise three times from large bulks of hot water (100°). The m. p. of th condensation product of aminoguanidine nitrate with pyruv acid is given in the literature (*loc. cit.*) as 206°, but our product di not melt at 350°, doubtless owing to polymerisation during th treatment with hot water (Found for the anhydrous substance: 22·7; H, 4·5. Calc.: C, 23·2; H, 4·35%). In calcium propiona cultures fermented as described above, the pyruvic acid formed w found to diminish after 2 or 3 days and a little later the solutio gave positive naphtharesorcinol tests indicative of the presence

glyoxylic acid. The latter could not be characterised owing to the smallness of the amounts present and to interference from traces of pyruvic acid which still persisted in the media.

Fermentation of Lactic Acid. Detection of Pyruvic Acid.—A solution of Kahlbaum's calcium lactate (50 g.) in 2500 c.c. of solution M was sterilised, inoculated, and incubated at 32°. After 10 days a sample (25 c.c.) of the medium gave a faint red coloration when treated at 0° with a few c.c. of a benzenediazonium chloride solution, followed by sodium acetate. This coloration was much deeper when the test was performed after 12 days, but no solid condensation product separated. The culture medium was then filtered and treated with 15 g. of aminoguanidine acetate and 5 c.c. of glacial acetic acid. After 48 hours the precipitate was washed with cold water. The mother-liquor on strong cooling yielded another smaller crop and the total precipitate (1·71 g.) was recrystallised successively from large bulks of hot water (100°) and boiling methyl alcohol. A sample did not melt at 350° (Found: C, 33·3; H, 5·6. Calc.: C, 33·3; H, 5·6%). A quantity of the tripolymeride, $[CO_2H\cdot CMe{:}N\cdot NH\cdot C(NH_2){:}NH]_3$ (*loc. cit.*), made for purposes of comparison was identical in physical properties with the derivative under investigation.

In another experiment in which calcium lactate (10 g.) in solution M (500 c.c.) was fermented as above, the liquid yielded a positive test for pyruvic acid on the seventh day. The whole of the solution was at once filtered and treated with *p*-nitrophenylhydrazine (2 g.), dissolved in a mixture of glacial acetic acid (5 c.c.) and water (20 c.c.). After 24 hours the precipitate (1·0 g.) was recrystallised three times from ethyl alcohol; it then had m. p. 221°, alone or mixed with authentic pyruvic acid *p*-nitrophenylhydrazone (m. p. 221°) (Found, by micro-analysis: C, 49·0; H, 4·2. Calc.: C, 48·4; H, 4·0%).

Fermentation of Lactic Acid. Isolation of Oxalic Acid.—In the previous experiment, the mixture of mycelium and traces of insoluble matter which remained when the calcium lactate medium had been filtered was washed with water and extracted several times with warm dilute hydrochloric acid. The combined extracts were filtered, neutralised exactly with ammonia, acidified with acetic acid, and again filtered. This procedure removed all the inorganic constituents of solution M which are soluble in acetic acid. The small residue on the filter, presumably calcium oxalate, was dissolved in a little dilute hydrochloric acid, and the solution was neutralised with ammonia and acidified with acetic acid; the small amount of white precipitate obtained reduced potassium permanganate in dilute acidified solution (Found: CaO, 44·0. Calc.: CaO, 43·75%).

Fermentation of Pyruvic Acid. Detection of Ethyl Alcohol.—Pure sterile calcium carbonate (1 mol.) in sterile water was treated with freshly fractionated pyruvic acid (2 mols.). When neutralisation was completed the solution was diluted with a sterile aqueous solution of the necessary inorganic salts to give 1000 c.c. of medium containing 10 g. of pyruvic acid (as calcium salt). It was inoculated and incubated at 26° for 28 days; a test portion then yielded a distillate, which gave a strong iodoform reaction but contained no acetaldehyde, since the test with piperidine and sodium nitroprusside (Rimini, *Z. anal. Chem.*, 1904, **43**, 517) and other colour reactions were negative. The whole culture was then very carefully distilled and redistilled. The second distillate (100 c.c.) was treated with sodium dichromate (30 g.) and concentrated sulphuric acid (15 c.c.), and the mixture heated cautiously. The vapours were passed through two spiral-condensers and the distillate (30 c.c.) was collected in a receiver at 0°. A small portion of the distillate, when treated with a few drops of a dilute aqueous solution of piperidine and 0·25 c.c. of a very dilute aqueous solution of sodium nitroprusside, gave the distinct blue coloration characteristic of acetaldehyde (*loc. cit.*). The remainder of the distillate was treated with 1 g. of 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (dimethyldihydroresorcinol) (Neuberg and Reinfurth, *Biochem. Z.*, 1920, **106**, 286) dissolved in a little ethyl alcohol (free from acetaldehyde), and the resulting clear solution was kept at room temperature. The crystals that had separated after 48 hours were washed with cold water, dried in a vacuum, and dissolved in ethyl alcohol (10 c.c.); the solution was poured into cold water (200 c.c.). After repetition of this procedure and drying, the substance had m. p. 140° and did not depress the m. p. (140°) of an authentic specimen of aldomedon. Yield, 0·31 g. (Found: C, 70·4; H, 8·4. Calc.: C, 70·6; H, 8·5%).

Fermentation of Lactic Acid. Detection of Ethyl Alcohol.—A sterile solution of 50 g. of lactic acid (as calcium salt) in 2500 c.c. of solution M was inoculated and incubated at 26° for 28 days. The whole of the solution was then distilled, and the distillate oxidised as described above. A portion of the distillate from the oxidation mixture gave a positive colour test for acetaldehyde by Rimini's method (*loc. cit.*). Treatment of the rest of the distillate with dimethyldihydroresorcinol gave a very small amount of a crystalline precipitate, insufficient for analysis. It had m. p. 138·5° when alone and 139° when in admixture with an authentic specimen of aldomedon (m. p. 140°).

The authors' thanks are offered to Dr. F. L. Pyman, F.R.S., who gave every facility for the carrying out of this work, to Dr. F.

Challenger for a valuable suggestion relative to the characterisation of lactic acid, and to the Research Fund Committee of the Chemical Society for a grant which defrayed part of the cost.

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CX.—*A New Synthesis of 4-Amino-3-hydroxyphenylarsinic Acid.*

By ISIDORE ELKANAH BALABAN.

THE ten isomeric aminohydroxyphenylarsinic acids have been prepared, for the most part by Fourneau and his collaborators (*Ann. Inst. Pasteur*, 1923, **37**, 551; 1926, **40**, 933), who have also examined their trypanocidal action on infected mice.

The methods of preparing 4-amino-3-hydroxyphenylarsinic acid ($C/T = \frac{1}{2}$; for definitions, see King and Murch, J., 1924, **125**, 2596) from 3-nitro-4-aminophenylarsinic acid (Benda, *Ber.*, 1911, **44**, 3579) and from 5-aminobenzoxazolone (Cassella and Co., U.S.P. 1,539,798–9) give poor yields, and attempts to use 2-methylbenzoxazole and 2-nitro-5-aminophenol for the purpose have been unsuccessful.

4-Amino-3-hydroxyphenylarsinic acid can, however, be readily prepared by the following series of reactions. The mixture of 4-nitro- and 6-nitro-chloroacetanilides obtained by the nitration of *m*-chloroacetanilide, on hydrolysis with 25% sulphuric acid, gives the corresponding chloronitroanilines, which are readily separable by means of their difference in basicity. 3-Chloro-4-nitroaniline undergoes the Bart–Schmidt reaction to give 3-*chloro*-4-*nitrophenylarsinic acid* in 45% yield, and this acid, on boiling with 25% aqueous sodium hydroxide, furnishes 4-*nitro*-3-*hydroxyphenylarsinic acid*, which on reduction with glucose yields 4-amino-3-hydroxyphenylarsinic acid.

3-*Chloro*-6-*nitrophenylarsinic acid*, prepared from 3-chloro-6-nitroaniline, undergoes dearsenication on treatment with alkali, *p*-nitrophenol being formed. 3-Chloro-6-aminophenylarsinic acid, obtained from it by reduction, has been briefly described by Benda (*Ber.*, 1909, **42**, 3622); when heated with chloroacetamide on the water-bath, it gives 6-*glycineamide*-3-*chlorophenylarsinic acid*.

Attempts to prepare the corresponding arsinic acids from 2 : 3-dinitro-4-aminophenol, 2 : 4-dinitro-3-aminophenol and 4-aminopyrocatechol by the Bart–Schmidt reaction were unsuccessful.

The following results (mg./g. of mouse) were obtained in experi-

ments on mice infected with *Trypanosoma equiperdum*; the administration was *intravenous* (*i*), *subcutaneous* (*s*), or *oral* (*o*).

Phenylarsinic acids.	*T*.	*C*.	*C*/*T*.
4-Amino-3-hydroxy-(*i*)	2·0	0·6	1/3
,, ,, (*s*)	2·0	0·6	1/3
,, ,, (*o*)	6·0	0·4	1/15
4-Acetamido-3-hydroxy-(*i*)	1·0	0·5	1/2
,, ,, (*s*)	0·5	0·5	1
,, ,, (*o*)	1·0	0·4	1/2·5
3-Chloro-6-acetamido-(o)	*<0·05*	*>0·05*	—
6-Glycineamide-3-chloro-(*o*)	0·05	0·05	1
Arsenobenzenes.			
4 : 4′-Diamino-3 : 3′-dihydroxy-(*o*)	1·0	0·05	20
4-Amino-4′-acetamido-3 : 3′-dihydroxy-(*o*)	4·0	0·05	80
4 : 4′-Diacetamido-3 : 3′-dihydroxy-(*o*)	8·0	0·1	80
3 : 4′-Diamino-4 : 3′-dihydroxy-(*o*)	2·0	0·1	20
3 : 4′-Diacetamido-4 : 3′-dihydroxy-(*o*)	10·0	0·2	50

EXPERIMENTAL.

3-*Chloro*-4-*nitrophenylarsinic Acid*.—3-Chloro-4-nitroaniline (51·75 g.) was ground with concentrated hydrochloric acid (103·5 c.c.) and water (103·5 c.c.), diazotised at 0° (sodium nitrite, 21 g.; water, 63 c.c.), and added to copper arsenite solution (Lewis and Cheetham, *J. Amer. Chem. Soc.*, 1921, **43**, 2119). The mixture was stirred for ½ hour and then heated for ½ hour at 60°, and the filtered liquor was acidified (Congo-paper) with concentrated hydrochloric acid. The crystalline acid obtained (37·5 g.; yield, 45·0%) separated from 2*N*-acetic acid in long, irregular, pale yellow, anhydrous prisms, decomp. 200°, sparingly soluble in cold water, soluble in alcohol (Found: As, 27·1; N, 4·9; Cl, 12·9. $C_6H_5O_5NClAs$ requires As, 26·7; N, 5·0; Cl, 12·6%). The *barium* salt forms prismatic rods; the *calcium* and *magnesium* salts are amorphous.

4-*Nitro*-3-*hydroxyphenylarsinic Acid*.—A solution of 28·2 g. of the preceding acid in 4*N*-potassium hydroxide (300 c.c.) was boiled under reflux for 3 hours, filtered hot, and acidified with concentrated hydrochloric acid (Congo-paper). The crystalline acid obtained (19·2 g.; yield, 73%) separated from glacial acetic acid in pale yellow, anhydrous needles, sparingly soluble in water but readily soluble in alcohol (Found in substance dried at 100°: As, 28·3; N, 5·4. $C_6H_6O_6NAs$ requires As, 28·5; N, 5·3%). The *magnesium* salt is microcrystalline and the *barium* salt forms minute rods.

This acid (49 g.), dissolved in a hot solution of sodium hydroxide (52·5 g. in 175 c.c. of water), was reduced by glucose (42 g. in 140 c.c. of hot water) to 4-amino-3-hydroxyphenylarsinic acid (Benda, *loc. cit.*), which was isolated (30 g.; yield, 68%) after acidification, treatment with charcoal, filtration, and addition of solid sodium

acetate. This acid crystallises from $2N$-acetic acid in small, hexagonal, anhydrous prisms (Found: As, 31·7; N, 5·9. Calc.: As, 32·2; N, 6·0%).

The following arsenobenzenes, which are all yellow, amorphous powders and are all soluble in sodium hydroxide solution, were prepared at 55—60° by the well-known hydrosulphite method from the respective phenylarsinic acids or from mixtures of two of them. Bertheim (*Chem. Ztg.*, 1914, **38**, 756) has shown that when two different arsinic acids (1 mol. of each) are so reduced, a mixed arsenobenzene is obtained. The first three arsenobenzenes form soluble hydrochlorides: 4 : 4′-Diamino-3 : 3′-dihydroxyarsenobenzene (Benda, *loc. cit.*) (yield, 45%) (Found in material dried over sulphuric acid: As, 39·6. Calc.: As, 41·0%).

4-Amino-4′-acetamido-3 : 3′-dihydroxyarsenobenzene (yield, 49%) (Found: As, 35·2. $C_{14}H_{14}O_3N_2As_2$ requires As, 36·8%).

3 : 4′-Diamino-4 : 3′-dihydroxyarsenobenzene (yield, 43·7%) (Found: As, 39·9. $C_{12}H_{12}O_2N_2As_2$ requires As, 41·0%).

4 : 4′-Diacetamido-3 : 3′-dihydroxyarsenobenzene (yield, 37·5%) (Found: As, 32·0. $C_{16}H_{16}O_4N_2As_2$ requires As, 33·3%).

3 : 4′-Diacetamido-4 : 3′-dihydroxyarsenobenzene (yield, 40·6%) (Found: As, 32·4. $C_{16}H_{16}O_4N_2As_2$ requires As, 33·3%).

4-Acetamido-3-hydroxyphenylarsinic acid, which has also been prepared by Benda (*Ber.*, 1914, **47**, 995), was obtained (yield, 94·5%) in almost colourless, diamond-shaped plates on acidification of an alkaline solution of the acid. It is almost insoluble in hot water and alcohol and very sparingly soluble in 50% acetic acid, but is readily soluble in cold 80% formic acid (Found: As, 27·4; N, 5·1. Calc.: As, 27·4; N, 5·1%). The *magnesium* salt is amorphous and the *sodium* salt crystallises in fine colourless needles from alcohol.

2-Nitro-4-acetamido-3-hydroxyphenylarsinic acid, prepared according to Benda, crystallises from much boiling water in long, red, glistening, hexagonal, anhydrous prisms, and from glacial acetic acid, in which it is sparingly soluble, in rods. It is moderately easily soluble in alcohol (Found: As, 23·1; N, 8·4. Calc.: As, 23·4; N, 8·7%). The *calcium* salt crystallises in bunches of needles; the *magnesium* and *barium* salts are amorphous.

2-Nitro-4-amino-3-hydroxyphenylarsinic acid, obtained according to Benda (*loc. cit.*), crystallises from water, in which it is appreciably soluble, in long, red, glistening, boat-shaped plates; these, on drying at 100°, change to a brown *monohydrate*, the water in which is not lost at 110° (Found in material dried at 110°: As, 25·1; N, 9·8. $C_6H_7O_6N_2As,H_2O$ requires As, 25·3; N, 9·5%). It is soluble in alcohol and moderately easily soluble in glacial

acetic acid, from which it crystallises in small prisms. The *magnesium* salt is amorphous when precipitated from an ammoniacal solution of the acid.

2-*Amino-4-acetamido-3-hydroxyphenylarsinic Acid*.—The nitroacetamidohydroxy-acid described above (22 g.) was reduced at 30° by ferrous sulphate according to Jacobs, Heidelberger, and Rolf (*J. Amer. Chem. Soc.*, 1918, **40**, 1581), 14·6 g. (yield, 73·8%) of crystalline material being obtained. The *acid* crystallises from boiling water (solubility, 1 in 22) in long, colourless, rectangular, anhydrous prisms (Found: As, 26·1; N, 9·7. $C_8H_{11}O_5N_2As$ requires As, 25·9; N, 9·6%). It is soluble in excess of 2*N*-hydrochloric acid, readily soluble in cold 80% formic acid, moderately easily soluble in glacial acetic acid, but almost insoluble in alcohol. On treatment with nitrous acid it gives an insoluble *diazo-oxide*, which crystallises in yellow, quadrilateral plates and does not couple with sodium β-naphthoxide. The *calcium* salt is microcrystalline and the *magnesium* salt amorphous.

2 : 4-*Diacetamido-3-hydroxyphenylarsinic acid*, prepared from the above by acetylation in alkaline solution with acetic anhydride, crystallises from 2*N*-acetic acid, in which it is moderately easily soluble, in clusters of colourless, silky, anhydrous needles (Found: As, 23·1; N, 8·8. $C_{10}H_{13}O_6N_2As$ requires As, 22·6; N, 8·4%).

3-*Chloro-6-nitrophenylarsinic acid* was obtained from 3-chloro-6-nitroaniline by the Bart–Schmidt reaction (yield, 64·1%). It crystallises from water in anhydrous rods which shrink at 240° and melt at 250° (Found: As, 27·1; N, 4·8. $C_6H_5O_5NClAs$ requires As, 26·7; N, 4·8%). It is very sparingly soluble in glacial acetic acid, crystallising therefrom in long, colourless, rectangular prisms, and soluble in hot alcohol. The *magnesium* salt is amorphous.

On reduction with ferrous sulphate the acid gives an almost quantitative yield of 3-chloro-6-aminophenylarsinic acid (compare Benda, *Ber.*, 1909, **42**, 3622). This acid crystallises from water, in which it is moderately easily soluble, in long, colourless, rectangular, anhydrous prisms (Found: As, 30·0; N, 5·4. Calc.: As, 29·8; N, 5·6%). It is soluble in cold concentrated hydrochloric acid; the solution develops a bright red colour on diazotisation and treatment with sodium β-naphthoxide. The acid is readily soluble in 80% formic acid and sparingly soluble in alcohol and glacial acetic acid; it crystallises in clusters of needles from the last-mentioned solvent. The *calcium* salt forms rosettes of needles and the *barium* salt is amorphous.

3-*Chloro-6-acetamidophenylarsinic acid*, obtained on acetylation of the preceding acid, crystallises from water (solubility, 1 in 15)

in long, colourless, rectangular prisms (yield, 57·5%) (Found: As, 25·6; N, 5·1. $C_8H_9O_4NClAs$ requires As, 25·5; N, 4·8%). It is fairly readily soluble in glacial acetic acid and almost insoluble in alcohol. The *magnesium* salt is microcrystalline.

6-*Glycineamide-3-chlorophenylarsinic Acid.*—3-Chloro-6-amino-phenylarsinic acid (5 g.) in 2*N*-sodium hydroxide (15 c.c.) was heated on the water-bath for 2 hours with chloroacetamide (1·9 g.); on acidification, 5·3 g. (yield, 81·0%) of product were obtained. This *acid* dissolves to the extent of 1 part in 30 parts of boiling water and crystallises in fine, anhydrous needles, m. p. 195° (decomp.) (Found: As, 24·3; N, 9·0. $C_8H_{10}O_4N_2ClAs$ requires As, 24·3; N, 9·1%). It is moderately easily soluble in glacial acetic acid and readily soluble in alcohol. The *magnesium* salt is microcrystalline and the *calcium* salt crystallises in glistening plates.

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CXI.—*An Examination of a Method of Estimating Iron and Sulphur in Sulphides of Iron.*

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IT has been stated that neutral aqueous copper sulphate solution dissolves the whole of the iron from iron sulphides (Wright, J., 1883, **43**, 162), and an analytical procedure based upon this statement has been described (Weyman, *Gas J.*, 1920, 310) whereby the unweighed iron sulphide is treated with warm aqueous copper sulphate, iron is determined in the filtrate, and sulphur is estimated indirectly in the residue by dissolving it in nitric acid and precipitating copper electrolytically. As such a method appeared to be of value in connexion with another research (see following paper), it was re-examined because there appeared to be two possible sources of error: (1) it is always difficult to secure complete conversion of one solid into another by the above means, and (2) it is not impossible that free hydrogen sulphide might exist in presence of copper sulphate.

Moist ferrous sulphide, prepared by precipitating slightly acid aqueous ferrous sulphate with a freshly made solution of ammonium monosulphide, and giving on analysis a ratio Fe : S = 55·8 : 32·1, was treated in a series of experiments with 30 c.c. of cold 10% aqueous copper sulphate solution with or without the addition of sulphuric acid. The mixture was heated slowly to 100° in a water-bath and digested at that temperature for 2 hours. The residual

solid was then filtered off and washed, and its copper was determined electrolytically and iron gravimetrically, with the results shown in the table.

No.	H_2SO_4 (g. per 100 c.c. of soln.).	FeS taken, g.	% Total S converted into CuS.	% Total S unconverted into CuS.	% Total S unaccounted for (by diff.).
1	0	0·1370	86·96	16·87	− 3·83
2	0	0·1406	80·63	19·96	− 0·59
3	0·92	0·1875	73·41	4·64	21·95
4	0·92	0·1298	69·53	7·12	23·35
5	1·84	0·0825	84·37	4·53	11·10
6	1·84	0·2132	69·36	7·07	23·57
7	3·68	0·2320	69·63	8·73	21·64
8	3·68	0·2623	65·67	3·02	31·31

It will be seen that up to 85% of the sulphur present forms cupric sulphide, but that the conversion is greatly retarded by acid even at relatively low concentrations. The sulphur unaccounted for is small at low acid concentrations (and even negative in the absence of acid, probably owing to the formation of insoluble basic copper salts), but increases with increasing acid concentration to about 10—30%. Addition of ammonia to the acid filtrate produced a considerable black precipitate, whence it appears that the missing sulphur was probably present in solution as hydrogen sulphide through displacement to the left of the equilibrium: $H_2S + CuSO_4 \rightleftharpoons CuS + H_2SO_4$. The evolution of hydrogen sulphide was not detected during the course of any of these experiments.

A further series of experiments on fused ferrous sulphide, in the form of a fine powder passing a 200-mesh sieve, showed that in the absence of free acid there was very little reaction between the sulphide and the copper sulphate solution, and that with varying concentrations of acid results both low in sulphur and discordant amongst themselves were obtained.

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CXII.—*The Reaction between Monohydrated Ferric Oxide and Hydrogen Sulphide at* 100°.

By THOMAS GIBSON PEARSON and PERCY LUCOCK ROBINSON.

THERE exists a considerable literature on the production of ferric sulphide by wet methods and on the use of oxides of iron and other metals for purifying coal gas, but little work has been done on the simple reaction concerned. As it has nowhere been summarised the following brief résumé is given.

The earlier workers found that the product of the reaction

hydrogen sulphide on hydrated ferric oxide contained more sulphur than does ferric sulphide (Deiche, *J. Gasbel.*, 1868, 106; Cox, *ibid.*, 1869, 584; Brescius, *ibid.*, 1869, 62), its exact nature being uncertain; Wright (J., 1883, **43**, 156) regarded it as a mixture of ferrous and ferric sulphides with free sulphur; Gedel (*J. Gasbel.*, 1905, **48**, 400, 432) reported that in alkaline conditions it was wholly ferric sulphide, whilst in acid conditions it was a mixture of the mono- and di-sulphides with free sulphur; and Allen, Crenshaw, Johnston, and Larsen (*Z. angew. Chem.*, 1912, **76**, 215) found it to be a mixture of ferrous sulphide and sulphur, the former being completely soluble in cold dilute hydrochloric acid after the sulphur had been extracted with ammonium polysulphide. Using a suspension of ferric hydroxide in water and excluding air, Mecklenburg and Rodt (*Z. anorg. Chem.*, 1918, **102**, 130) identified the dried product as ferric sulphide, which was pyrophoric if suddenly exposed to air but could be stabilised by treatment with carbon dioxide and then gained weight slowly in air, rather by absorption of moisture than by oxidation. After this treatment the material yielded a considerable amount of sulphur on extraction with carbon disulphide, and 31% of the residue was insoluble in dilute hydrochloric acid, whereas the original product contained but 2% of extractable sulphur and was wholly decomposed by acid, yielding $2FeCl_2 + 2H_2S + S$. Most of these workers agree in finding about 2% of free sulphur in the product.

The reactivity of ferric hydroxide towards hydrogen sulphide varies with the temperature (between 100° and 800°) at which the hydroxide has been dried (Weyman, *J. Soc. Chem. Ind.*, 1918, **37**, 333T), and this variation has been explained in terms of the difference in molecular state (Nicolardot, *Ann. Chim. Phys.*, 1905, **6**, 334).

An attempt has been made (Rodt, *Z. angew. Chem.*, 1916, **92**, 422) to explain these varying results by (i) the ready conversion of moist ferric sulphide to oxide and free sulphur by air; (ii) the change of ferric sulphide into a mixture of ferrous sulphide and iron disulphide on standing; (iii) the possible formation of water-soluble colloidal sulphur when ferric sulphide is dissolved in dilute hydrochloric acid, which would cause it to be mistaken for the ferrous salt. It seems probable, however, that differences arise chiefly because the course of the reaction actually varies in different experiments, and the few analyses recorded have been insufficient to exhibit the variation fully or to establish an average course for the reaction.

The most serious attempt to investigate the reaction appears to be that of Wright (*loc. cit.*), who prepared pure monohydrated ferric

oxide, treated it at laboratory temperature with pure hydrogen sulphide, and dried the product in hydrogen at 100°. In nine runs the increase in weight on sulphidation was estimated, and the water produced was collected and weighed. In four of these cases the dry solid residue was also analysed : it was black, intensely pyrophoric, soluble in hot aqueous potassium cyanide, and completely decomposed by aqueous cupric sulphate or silver nitrate solutions (compare Robinson, Sayce and Stevenson, preceding paper). Wright's data for the "sulphide"/hydroxide ratio and the percentage conversion to "sulphide" calculated therefrom are given in Cols. 2 and 3 (*a*) of Table I, but these conversions are open to doubt, for those now calculated from the total increase in weight of the reaction tube and drying tube [Col. 3 (*b*)] are much smaller and more variable.

TABLE I.

Run.	"Sulphide"/Hydroxide.	% Oxide converted, as calculated from (*a*) ratio.	(*b*) total increase.	% S in "sulphide."
6	1·167	100·4	77·5	—
2	1·163	100·0	92·5	43·78
3	1·158	99·6	86·5	40·05
1	1·134	97·6	86·1	—

From the foregoing data and from determinations of free sulphur (in four cases) Wright concluded that there were two reactions, (A) $Fe_2O_3,H_2O \longrightarrow Fe_2S_3 + 4H_2O$, and (B) $Fe_2O_3,H_2O \longrightarrow 2FeS + S + 4H_2O$, the second applying to 17—30% of the hydrated oxide.

Evidently the subject needs further investigation, but the inquiry is complicated by the difficulty of carrying the reaction to completion, by the complex nature of the product, and by secondary reactions in, and possibly between, the substances primarily produced. It seemed probable that the course of the reaction varies within certain limits, and that the best method of attack would be repeated sulphidation and analysis.

In this investigation ferric oxide of known hydration was treatec with hydrogen sulphide at laboratory temperature or at 100° ir about 50 distinct runs, the ratio "sulphide"/hydrated oxide bein computed in each case. Qualitative tests were made on the "sulph ide" to determine its properties, but the main part of the wor consisted in estimating, in the product produced at 100°, one o other of the following : (i) the total iron and sulphur, (ii) the sulph soluble in carbon disulphide, (iii) the material insoluble in 10 hydrochloric acid, (iv) the material insoluble in boiling saturat aqueous potassium cyanide, (v) the sulphur liberated by 10 hydrochloric acid. The results disclose an unexpected variati

in the course of the reaction, which may explain the discrepant results of earlier workers; nevertheless, the mean values derived from analytical data may serve to indicate the probable nature and extent of the fundamental reactions involved.

EXPERIMENTAL.

Materials and Apparatus.—The hydrated oxide was prepared by diluting a solution of basic ferric chloride, free from metallic impurities, in hydrochloric acid with distilled water so that the concentration of acid was about 10%, and adding this solution with stirring to cooled aqueous ammonia, free from carbonate and organic impurities. The precipitate was separated from the supernatant liquor, repeatedly washed by decantation with 5% aqueous ammonia, collected on a Buchner funnel, and washed several times with large quantities of distilled water. The drained hydroxide was then dried at 100° for 4—5 days. Two lots of material were prepared [Found: Fe_2O_3, (1) 88·41, (2) 89·17. Calc. for Fe_2O_3,H_2O: Fe_2O_3, 89·87%]. Neither preparation contained more than a trace of volatile material other than water. As such oxides are distinctly hygroscopic, they were preserved in stoppered bottles kept in a desiccator. Before bottling they were ground and sieved (150—200 mesh).

The hydrogen sulphide, prepared by the action of hydrochloric acid on ferrous sulphide, was washed with water in three Drechsel bottles, and dried by passage through a large, wide bottle, containing fused calcium chloride, and a tower filled with the same material. The hydrogen, prepared from arsenic-free zinc and hydrochloric acid, was washed with water in three Drechsel bottles, and dried by passage through a tower packed with calcium chloride and through about 3 feet of glass tubing containing a liberal supply of phosphorus pentoxide spread on glass wool.

The two gas trains, which were strictly air-tight, met in a Y-piece of glass, with taps on two of the limbs; the gases passed *via* the third limb to the reaction tube, a U-tube with tap-stoppers, and thence through a length of glass tubing to a bubbler containing water, which marked their passage and prevented backward diffusion of air. The procedure consisted in washing out each train thoroughly with its respective gas, cleaning and drying the U-tube, slightly greasing its stoppers, sweeping it free from air with hydrogen and weighing it, charging the tube with oxide by means of a dry funnel which was not allowed to touch the tap-grease, and, finally, again sweeping with hydrogen and weighing. Hydrogen was then passed for upwards of 45 minutes to ensure the complete removal of the air admitted to the third limb of the Y-tube and the connecting tubes during the last operation. This was followed by the passage of

hydrogen sulphide, the reaction tube being kept in constant motion during the first $\frac{1}{2}$ hour, to minimise the caking of the material. From this point the procedure varied and is given below.

The Reaction at Laboratory Temperature, producing a Hydrated Sulphide.—During runs 5—8 (Table II) the reaction tube was suspended in a beaker of water at laboratory temperature, and the product dried by passing hydrogen for the time stated. As the calculated ratio $Fe_2S_3/Fe_2O_3,H_2O$ is 1·170, the ratios observed, which were substantially unchanged by the passage of dry hydrogen over a long period, suggest that a hydrated sulphide was produced; this idea is supported by the fact that water was at once evolved when the temperature was raised to 100°. The data for the ratio of "sulphide" to water liberated are too variable to show the formula of the hydrate, and it is not known in what proportion the various sulphides are present, or how much, if any, of the liberated water is derived from unconverted oxide which has suffered further hydration by the moisture produced in the reaction. (This matter is receiving further attention, and an attempt is being made to isolate the hydrate.) Runs 9—15 indicated that the degree of conversion may be very variable, and this was borne out by runs 16—22 (not shown), where the product produced in precisely the same way was far from uniform in each case, and gave values fo sulphur varying from 43% (almost Fe_2S_3) to 20% in different run It is believed that this was due principally to protective caking the product by the water produced, and that under these conditio a material of uniform composition could not be attained. Th authors are unable to account for the serious discrepancy betwe these results and those of Wright (*loc. cit.*), and of Weyman (*loc. cit* who reports a conversion into material of the composition of fer sulphide.

TABLE II.

Run.	Oxide (g.).	H_2S (hours).	H_2 (hours).	"Sulphide" / Oxide.	H_2 at 100° (hours).	"Sulphide" / Oxide
5	2·3260	22	4	1·247		
6	2·3437	17	34	1·235		
7	5·1543	17	17	1·242		
8	2·4509	17	12	1·253		
9	1·7499	72	6	1·352	4·0	1·165
10	1·2900	17	8	1·280	2·3	1·160
11	2·4068	17	8	1·300	3·0	1·091
12	1·9096	17	4	1·216	3·0	1·102
13	3·0327	20	19	1·417	2·5	1·124
14	1·6252	17	0	1·217	3·0	1·072
15	1·0704	17	3	1·215	3·0	1·06[illegible]

The Reaction at 100°.—In the following runs the reaction carried out at 100° by immersing the U-tube in boiling wa After the tube had been charged and the air removed as descr

above, hydrogen sulphide was passed for 3 hours, followed by dry hydrogen for 30 minutes. The product, although not actually pyrophoric, usually became hot on exposure to air and increased in weight sufficiently to vitiate analysis. Dry air was therefore passed over it for 30 minutes in order to stabilise the weight, and the tube was then filled with hydrogen and reweighed. Thus the amount of the unoxidised "sulphide" could be computed. The sulphide was analysed for iron by weighing the ferric oxide left on ignition to constant weight, and for sulphur by oxidation to sulphate and weighing as barium sulphate. Oxidation was effected by both a dry and a wet method: (1) About 0·35 g. of sulphide was intimately mixed with fusion mixture and potassium nitrate in a platinum crucible, covered with a further quantity of these materials, 3 g. in all of each being used, and the upper edge of the crucible was gently heated until reaction began; when reaction had apparently ceased, the temperature was raised sufficiently to keep the mixture molten for about 15 minutes. (2) In the wet method fuming nitric acid and bromine were used. The results by the two methods were in excellent agreement. The dry method was tested on pyrites and on laboratory monosulphide; with the former it gave excellent results, but for the latter it was practically useless. In all cases blanks were carried through on the materials used.

TABLE III.

Run.	Oxide (g.).	"Sulphide" / Oxide.	Fe in sulphide, %.	S in sulphide, % (found, and mean).	Fe + S, %.
23	1·1819	1·167	53·98	42·74, 42·91; 42·83	96·81
24	1·0553	1·151	54·95	40·72, 39·96; 40·34	95·29
25	1·3369	1·171	53·78	43·51, 43·35; 43·43	97·21
26	1·3297	1·167	53·32	42·10, 41·51; 41·81	95·13
27	1·2958	1·177	53·06	43·75, 42·25; 43·00	96·06
29	1·1539	1·173	53·96	42·53, 39·29; 40·91	94·87
30	0·9349	(1·213)	52·06	43·40, 43·40; 43·40	95·46
31	0·5224	(1·191)	52·78	43·16, 43·06; 43·11	95·89
32	0·7654	1·163	52·64	41·20, 42·12; 41·66	94·30
	Mean	1·167 *	53·39	42·28	95·67
				$O + H_2O$ (by diff.) =	4·33

* Nos. 30 and 31 are omitted because of a short drying period.

Table III shows that the ratio "sulphide"/oxide is much more constant than that found previously, and, though variations of about 3% may be found in one sample of sulphide, its composition is much more uniform. The total sulphur and iron are 3—5% below 100%: this is probably due to incomplete conversion and to the retention of some water by the material. It is, however, clear that the procedure employed above gives a readily reproducible product of reasonably uniform composition.

Sulphur Soluble in Carbon Disulphide.—After the ratio "sulphide"/

oxide had been determined, the U-tube was again attached to the train and, with hydrogen passing, the stop-cock farthest from the source of hydrogen was taken out and the tap-grease removed from the mouth of the tube with a cloth moistened with ether. A cork carrying a tap-funnel was now fitted to the tube, and 20 c.c. of carbon disulphide (thrice-distilled material, without objectionable odour, and leaving no residue on evaporation) were run in and allowed to stand thus, with frequent shaking, for 1 hour. The solution was carefully decanted through an ashless filter-paper, and the residue was similarly treated with two further lots of solvent. A positive pressure, or a stream, of hydrogen, according to circumstances, prevented ingress of air during the whole operation. The extracted residue is pyrophoric when dry. The combined filtrates were evaporated to dryness and the sulphur estimated by weighing, or by conversion to barium sulphate, or both. Table IV gives the results, and shows that sulphur was produced in each run, and as this might have been due to atmospheric oxygen retained by the hydrated oxide, in runs 52 and 53 the hydrogen used to displace the

TABLE IV.

Run.	Oxide (g.).	"Sulphide" / Oxide.	S sol. in CS_2 in "sulphide," %.
33	0·7806	1·200	1·93
34	0·7912	1·159	2·52
35	0·6633	1·167	2·41
36	0·8991	1·174	2·53
37	1·3796	1·168	1·96
52	0·4532	1·150	3·17
53	0·2895	1·140	2·55
			Mean 2·44%

air was passed for 3 hours, instead of the usual 45 minutes, in order to reduce the residual oxygen to a minimum, but this did not diminish the yield of sulphur.

Material Insoluble in 10% *Hydrochloric Acid* (*Iron Disulphide*).—The acid, about 20 c.c., was added exactly as described for carbon disulphide. The tube, with both stop-cocks removed, was then immersed above the acid level in a beaker of boiling water and gently shaken until gas ceased to be evolved. The residue was completely transferred to a filter-paper, well washed with warm 10% hydrochloric acid, and finally ignited to ferric oxide. Analysis of thi residue in a number of cases (after its extraction with carbon disulph ide, see below) showed it to be entirely due to the iron disulphid present in the product, and results calculated on this assumptio are given in Table V; the values vary considerably, but they ten to be about 7%.

TABLE V.

Run.	Oxide (g.).	"Sulphide" / Oxide	Fe_2O_3.	FeS_2, calc. from Fe_2O_3 (as % of "sulphide" in each case).	S liberated.
38	0·2716	1·172	4·52	6·80	
39	0·4135	1·165	4·32	6·49	
41	0·1777	1·165	9·33	14·03	
42	0·2512	1·166	4·71	7·07	
49	0·3397	1·153	2·86	4·30	13·46
50	0·7405	1·151	8·64	12·99	12·49
51	0·7657	1·180	3·19	4·79	13·20
52	0·4532	1·150	4·95	7·44	
53	0·2895	1·140	4·37	6·57	13·40
		Mean	5·21	7·83	13·14

Material Insoluble in Concentrated Potassium Cyanide Solution (Iron Disulphide and Unchanged Hydrated Oxide).—Saturated potassium cyanide solution was added to the "sulphide" by the same means and with the same precautions as above. The tube was well shaken, its contents were transferred to a beaker containing a further 200 c.c. of solution, and the liquid was gently boiled for 6 hours. It was then diluted, and the residue collected on a filter-paper, well washed, and ignited to ferric oxide. No definite information was found in the literature as to the solubility of the various sulphides in potassium cyanide solutions, but a reinvestigation showed that whilst ferrous and ferric snlphides dissolved, iron disulphide was apparently insoluble under the conditions of the experiment. Thus it is assumed that the residue contained only the unaltered hydrated oxide and the disulphide previously shown to be present.

TABLE VI.

Run.	Oxide (g.).	"Sulphide" / Oxide	Fe_2O_3 as % of "sulphide."
44	0·2510	1·171	6·84
45	0·7283	1·144	9·87
46	0·2830	1·168	18·10
47	0·6942	1·169	8·78
48	1·0920	1·121	9·15
54	0·2904	1·127	19·44
55	0·1967	1·168	11·24
		Mean	11·93

Table VI gives the weight of the ferric oxide (expressed as a percentage of the "sulphide") resulting from the ignition of the residue, and it is obvious that the mean valne is about twice the mean value of the same oxide in Table V, the difference of 6·72% Fe_2O_3 being ascribed to 7·48% of unaltered Fe_2O_3,H_2O. Again, the products of various runs differ considerably, probably because of variation in the proportion of disulphide rather than in the unattacked hydrated oxide.

Sulphur Liberated on Dissolution of "Sulphide" in Hydrochloric Acid.—It has already been pointed out that there was no evident liberation of sulphur when the products were treated with 10% hydrochloric acid, but the black residue was more bulky than would be anticipated from the comparatively small amounts of oxide left after ignition. When washed with pure alcohol and ether, to remove water, and then extracted with pure carbon disulphide, it yielded sulphur, which was estimated by weighing and by conversion into barium sulphate. The results are given in the last column of Table V, and it is evident that they include in each case the "free" sulphur mentioned in Table IV. They appear to be remarkably concordant when compared with the figures for disulphide plus unchanged material; it is indeed possible that the variation which does exist is brought about by variation in "free" sulphur present before the addition of hydrochloric acid. When this "free" sulphur is deducted the mean sulphur liberated becomes 10·70%, and from this one may calculate the percentage of ferric sulphide to be 69·40% on the assumption that it yields $2FeCl_2 + 2H_2S + S$ on treatment with hydrochloric acid.

Discussion of Results.

The black product of this reaction tends to oxidise when exposec to air, but is not pyrophoric until it has been extracted with carbor disulphide, indicating that the particles are coated with a film o free sulphur which, by preventing actual contact with air, gives th material an apparent stability. The ratio "sulphide"/oxide corre sponds very closely with that required for a complete conversio into ferric sulphide (see Table III, where the oxide was fresh, th later discrepancies being due to the further hydration of the oxide) the material is partly soluble in dilute hydrochloric acid with th evolution of hydrogen sulphide, whilst the black residue contai sulphur extractable with carbon disulphide, although the supe natant liquid is free from the opalescence usually associated with th liberation of that element. There is evidence of considerable variati in the course of the reaction, but its general nature may be deduc from the mean values shown above as set out in Table VII. T ferrous sulphide is calculated by assuming that the additional 3·56 sulphur required by the complete analysis of the material (s Table III; 53·39% of Fe requires 45·84% S, as compared wi 42·28%) existed as this compound, and the moisture is obtain by deducting 2·78 (= $3O + H_2O$ in 7·48% Fe_2O_3,H_2O, see p. 8 from 4·33 ($O + H_2O$ in Table III). It will be seen that all 1·5% is accounted for, the discrepancy being thrown entirely the iron by the method of calculation.

TABLE VII.

	%.	% S.	% Fe.
Free sulphur	2·44	2·44	—
Iron disulphide	7·83	4·18	3·65
Ferric sulphide	69·40	32·10	37·30
Ferrous sulphide	9·76	3·56	6·20
Fe_2O_3,H_2O unaltered	7·48	—	4·70
Moisture	1·55	—	—
Totals	98·46	42·28	51·85

Free sulphur is invariably found in this reaction under either dry or moist conditions; this has been ascribed by Wright (*loc. cit.*) to his reaction (B), and by Mecklenburg and Rodt (*loc. cit.*) to oxidation of hydrogen sulphide by residual adsorbed air. The evidence brought forward here supports the latter contention, for if Wright's reaction takes place, 13·38% ferrous sulphide would be required for the free sulphur alone, and none would be left to balance the disulphide which is most probably produced by the decomposition of ferric sulphide: $Fe_2S_3 \longrightarrow FeS_2 + FeS$. The 7·83% disulphide requires 5·74% ferrous sulphide for equimolecular proportions, and thus the total ferrous sulphide required would be of the order of 19·12%. The conclusions are that (1) the free sulphur is due to oxygen adsorbed on the surface of the oxide, which appears to be unreduced by long washing with hydrogen, (2) the primary reaction leads to the production of ferric sulphide, and (3) some ferric sulphide decomposes with the formation of equimolecular proportions of disulphide and monosulphide. The discrepancy in the ratio of disulphide to monosulphide is probably due to the slight solubility in acid of the former when in a finely divided condition.

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CXIII.—*The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part II. The Hydrogenation of Conjugated Systems.*

By SERGUEY V. LEBEDEV and ANASTORIA O. YAKUBCHIK.

THE simplest example of a conjugated system is afforded by divinyl, $CH_2{:}CH{\cdot}CH{:}CH_2$; if any of the hydrogen atoms are replaced, the properties of the derivative depend upon the number, position, and character of the substituents introduced. One of us (Lebedev, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249) has shown how the

nature and position of the different substituents affect the tendency to polymerisation, and in this communication a study is made of their influence on the catalytic hydrogenation of the derivatives. The addition of hydrogen in the presence of metallic catalysts has substantial advantages over the usual addition reactions, for a study of the hydrogenation curves enables consecutive reactions to be differentiated and selective catalysis to be detected.

We have studied the hydrogenation of more than a dozen substances containing conjugated systems, and have noted three different types of reaction.

Type I. This, the simplest type, consists of two consecutive phases: (1) the addition of hydrogen exclusively in the 1 : 4-position with formation of an ethylenic derivative; (2) the addition, at a different rate, to the 2 : 3 double bond. The corresponding curve (Fig. 1) has two entirely separate sections, each representing the absorption of 1 mol. of hydrogen; it resembles the hydrogenation curve of a binary mixture of ethylenic substances of different degrees of substitution (see Part I; J., 1925, **127**, 417), and the break corresponds to the complete consumption of one of the active components, for, by interrupting the process at this stage, we get a homogeneous product with a double linkage in the 2 : 3-position. Processes of this kind *therefore agree with Thiele's rule.* To this type belong those substances in which all the four hydrogen atoms in the 1 : 4-position of divinyl are replaced by aliphatic radicals, *e.g.*, di*iso*butenyl, $CMe_2{:}CH{\cdot}CH{:}CMe_2$.

Type II. This is a very complicated type. The addition of hydrogen takes place in all the possible directions: 1 : 2, 3 : 4, and 1 : 4. This leads to the formation of two (for a symmetrical molecule) or three (for an unsymmetrical molecule) substances containing only one double linking. The process is complicated by the simultaneous formation of fully saturated molecules. Thus the hydrogenation curves of divinyl and of piperylene show thre sharply separated sections, and the isoprene curve shows fou The curves of this type differ characteristically from those of th first type in that the end of the addition of the first mol. of hydroge is not marked by any change in shape: this point does not coincid with a change in the number of the active components of the systen The change occurs considerably later: in the cases we have investi ated, it corresponds to the addition of 68—77% of hydrogen (1·36-1·54 mols.) and to the consumption of the conjugated system.

If the process is interrupted after the addition of 1 mol. hydrogen, a mixture of four substances is obtained in the case symmetrical molecules and of five in the case of unsymmetric

ones. For instance, isoprene at this stage has produced 30% of *iso*pentane, 12% of *iso*propylethylene, 13% of *as*-methylethylethylene, and 15% of trimethylethylene, 30% of isoprene being unchanged. Processes of this type *do not follow the theory of Thiele.* Of the substances we have investigated, the following belong to this type: divinyl, piperylene, di*iso*propenyl, isoprene.

Type III. We include this type in our review as a theoretically possible one, but we have not yet observed it, and possibly it is never completely realised. In this case, the addition of 2 mols. of hydrogen would take place simultaneously, or—what leads to practically the same result—the addition of 1 mol. is immediately followed by the much more rapid addition of a second. By interrupting the process at any time, a mixture of unchanged material and of completely saturated hydrocarbons should be obtained. The corresponding curves would show no break and would resemble those of simple ethylenic substances.

Paal (*Ber.*, 1912, **45**, 2221) suggested that conjugated systems are always hydrogenated in this way, and sought confirmation of this by examining the products obtained after the addition of 1 mol. of hydrogen to certain substances containing a conjugated system. He chose for this purpose piperine, piperinic acid, cinnamylidenemalonic acid and cinnamylideneacetone. We have studied the hydrogenation of piperinic acid and have found that the process does not belong to our third type, as supposed by Paal. Our results will be published later.

In the three diagrams of Fig. 1, the percentages of hydrogen absorbed are plotted as abscissæ, and the molecular composition of the mixture is given by the ordinates. The first and third types can be considered as distinct types; the second is a transition type, which includes any number of variations between the two limiting types. *In all three cases, when 1 mol. of hydrogen has been added (50% hydrogenation) the number of unchanged (conjugated) molecules is equal to the number of fully saturated molecules.* On the diagrams this is expressed by the fact that the line of the conjugated system and the line of the saturated compound cross each other at a point corresponding to 50% of hydrogen added. The continuation of the first line intersects the abscissa at a point A, which determines the moment when the whole conjugated system is consumed. We call this *the critical point of the hydrogenation of a conjugated system.* It is a characteristic point which determines fully the course of the process, and from a knowledge of its position it is possible to draw the complete diagram. Thus, it is seen from the diagram of Type II (Fig. 1) that the positions of the breaks B and C are determined by the condition (above) as to the two lines

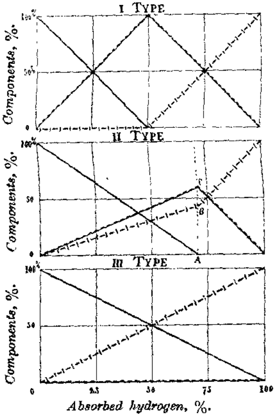
crossing on the 50% ordinate, in conjunction with the following data:

(1) Both points lie on the ordinate of the critical point A.

(2) AB + AC = 100.

The diagram of Type II shows A at 70% hydrogenation; this is the case with isoprene, but the diagram equally represents the hydrogenation process of any conjugated system whose critical point corresponds to 70% of hydrogenation.

FIG. 1.



——————— *Initial material (conjugated system).*
========= *Ethylenic substance.* —|—|—|— *Fully saturated substan*

The point A may be determined by several means:

1. Hydrogenation is carried up to 50%; the composition the hydrogenation mixture is then found by determining the amou of any one of the three compounds, these amounts being connect by the relations $a = b$ and $c = 100 - a - b$, where a is the co jugated system, b the fully saturated compound, and c the mo ethylenic compound. The diagram is then constructed on foregoing principles.

2. In many instances the critical point is easily determined f the hydrogenation curves of the pure substance containing

conjugated system and of its mixtures with different ethylenic substances; this occurs if the critical point corresponds to a well-defined break in the curve (see below and Fig. 2).

The three types we have dealt with comprise all the conjugated systems, but the classification of these systems will not be complete without including those cases in which 1 : 4-addition is not realised at all, the individual double linkings being hydrogenated independently. For the sake of completeness, we have gathered these cases into a special fourth type and we distinguish two varieties.

Type IV A. The double linkages differ in the degree of substitution, *e.g.*, as in CHR:CH·CH:CRR′. In this case the linkages are hydrogenated at different rates. The hydrogenation curve has a break corresponding to the addition of 50% of hydrogen, at which stage a homogeneous monoethylenic product is formed. This case agrees in the shape of the curve and in the diagram with Type I, but differs fundamentally in that no 1 : 4-addition products are formed. *The process does not follow Thiele's rule.*

Type IV B. The linkings are equal in the degree of substitution, as in CHR:CH·CH:CHR′, in which case they are hydrogenated simultaneously. The curve has the shape typical of homogeneous monoethylenic substances. When the product of 50% hydrogenation is examined, it is found to be a mixture of diethylenic, monoethylenic, and fully saturated compounds. The diagram in this case is somewhat similar to that of Type II, but the two cases differ inasmuch as 1 : 4-addition products are now absent.

In this paper we deal with the hydrogenation of isoprene.

EXPERIMENTAL.

The isoprene used was prepared by pyrogenetic decomposition of turpentine. The resulting isoprene and trimethylethylene were converted into their hydrobromides and isoprene dibromide was separated by fractional distillation, b. p. 80—82°/23 mm. The isoprene recovered by means of solid potassium hydroxide had b. p. 34·5°; $d_4^{20\cdot0°}$ 0·6803; $n_D^{20\cdot0°}$ 1·42207; $[R_L]_D$ 25·40 (Calc., 24·33; exaltation 1·07).

The isoprene was hydrogenated in the apparatus described in Part I (*loc. cit.*), alcohol being used as solvent, and platinum black, obtained by the method of Willstätter (*Ber.*, 1912, **45**, 1471), as catalyst; the bath temperature was in some tests 0°, and in others near to room temperature. The curves are plotted as in our former paper, the abscissæ giving time intervals and the ordinates showing the number of c.c. of hydrogen absorbed per ½ minute.

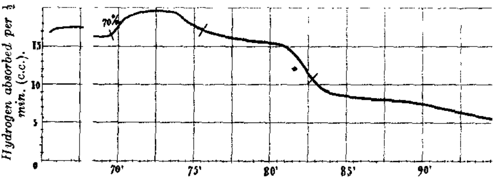
The hydrogenation of isoprene proceeds as shown in Curve 1, Fig. 3 (for details see Table IV, No. 2). The curve is horizontal

up to 70—71% of the hydrogen necessary to saturate both the *double linkages; in this section the velocity is uniform.* The *last 30% of hydrogen is added in a very peculiar way,* as shown on a larger scale in Fig. 2 (Table IV, No. 1), for which a large quantity of isoprene was used. At first the rate increases, and then it falls, showing two more or less horizontal sections. Thus the whole curve is divided into four parts, and it is obvious that isoprene is not hydrogenated at once to *iso*pentane, but that it passes through a range of intermediate stages. The amounts of hydrogen absorbed in the different sections, as calculated from Figs. 2 and 3, are :

Section	1	2	3	4
Hydrogen, %	70	8·5	9	12·5

The formula of isoprene $\overset{1}{C}H_2{:}\overset{2}{C}Me{\cdot}\overset{3}{C}H{:}\overset{4}{C}H_2$ indicates the following *possibilities for the process of hydrogenation* : (1) 1 : 2-*Addition*

FIG. 2.



of 1 *mol.*, *giving iso*propylethylene. (2) 3 : 4-*Addition of* 1 *mol.*, *giving as*-methylethylethylene. (3) 1: 4-*Addition of* 1 mol., *giving* trimethylethylene.

Thus the formula of isoprene would explain the presence of three sections of the curve; it will be shown later that the second, third, and fourth sections correspond to the above-named three amylenes. We must obviously attribute to the first section of the curve the hydrogenation of the isoprene itself in the three possible directions. The test with sulphur dioxide shows that isoprene is present all through the first section of the curve. At the last point of this section the isoprene disappears, *i.e.*, this point is "the critical point of hydrogenation of a conjugated system." Up to this point 70—71% *of hydrogen is added at a uniform rate*; *nevertheless, there is no doubt that in this part of the process several reactions* are occurring *simultaneously,* for there are produced *iso*pentane and three different amylenes, which, on the other side of the critical point, are hydrogenated *successively.* Thus we have to deal up

to the critical point with at least four reactions. The fact that all these four reactions are summed up in one common section of the curve may be explained by assuming that they are "conjugated" by a common initial material—the isoprene. As soon as this substance is consumed (at the critical point), several *successive* reactions start, and these proceed in accordance with the rules adduced in Part I (*loc. cit.*).

The Hydrogenation Process prior to the Critical Point.

25% *Hydrogenation.*—In order to study the process of the hydrogenation of isoprene up to the critical point we have investigated the products formed after the addition of 25%, 50%, and 70% of the hydrogen necessary for full saturation. The mixture of hydrocarbons produced by 25% and 50% hydrogenation contains isoprene, and it was therefore removed as a solid compound with sulphur dioxide. The further information necessary was obtained by a study of the hydrogenation of mixtures of ethylenic compounds.

To 12·011 g. of isoprene, 2110 c.c. of hydrogen (25% hydrogenation) were added (see Table IV, No. 3.) The reaction product was treated with sulphur dioxide,* and allowed to stand for 6 days. The separated hydrocarbons amounted to about 3·5 g., and when freed from the residue and from sulphur dioxide they boiled at 29—36°. They were analysed by the hydrogenation method.

For this purpose 0·85 g. of hydrocarbons was fully hydrogenated and required 173 c.c., whereas if the hydrocarbons consisted only of amylenes, 293 c.c. would have been required. The composition was therefore amylene 59%, *iso*pentane 41% (see Table IV, No. 5).

From the hydrogenation curve (Fig. 3, Curve 2), we can also determine the composition of the amylenes. The sections of the curve are marked by dashes, and later we show that the first section corresponds to *iso*propylethylene, the second to *as*-methylethylethylene, and the third to trimethylethylene. In Table I we give the amount of hydrogen absorbed in different sections of the curve and the calculated composition of the reduced product; and in

* The quantitative precipitation of isoprene is effected as follows: An alcoholic solution of the hydrogenation products is placed in a flask and saturated at 0° with sulphur dioxide; the flask is then closed. Precipitation soon commences and is complete in 2—3 days. If the concentration of isoprene is high, the contents of the flask form a colloidal mass. The liquid is distilled on a steam-bath into a vessel containing alkali at 0°, and the hydrocarbon layer which separates is again saturated with sulphur dioxide and left in a sealed vessel for some days in order to ensure that all the isoprene has been eliminated.

Table II is shown the composition of the original product of hydrogenation.*

TABLE I.

	25% Hydrogenation.		50% Hydrogenation.	
	H_2 absorbed, c.c.	Components, %.	H_2 absorbed, c.c.	Components, %.
*iso*Propylethylene	28	9·5 } 59	116	18 } 56·7
as-Methylethylethylene	28	9·5	119	18·7
Trimethylethylene	117	40·0	126	20
*iso*Pentane	0	41·0	0	43·3
Total	173	100	361	100

TABLE II.

Degree of hydrogenation.	25%.	50%.	70%.
Isoprene	64·5% (63·9%)	30%	0%
*iso*Pentane	14·5	30	40
*iso*Propylethylene	3·3	12	17
as-Methylethylethylene	3·4	13	18
Trimethylethylene	14·3	15	25
Total	*100*	*100*	*100*

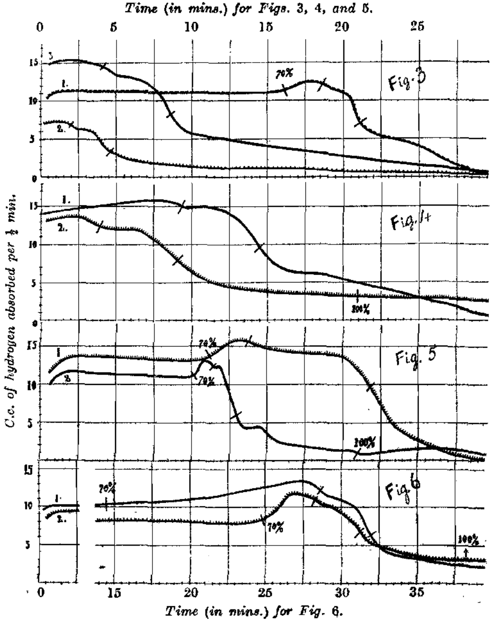
The isoprene was also estimated as a solid compound with sulphur dioxide. Two weighed samples of the 25% hydrogenation product were precipitated in an alcoholic solution by sulphur dioxide, and the dried residues weighed. These determinations gave 63·8 and 63·9% of isoprene, the latter value being that in parentheses in Table II.

50% *Hydrogenation.*—To 14·9 g. of isoprene, 5180 c.c. (1 mol.) of hydrogen were added (see Table IV, No. 4). The hydrogenation product was freed from isoprene as described above, and kept saturated with sulphur dioxide for 2 months. When freed from the residue, washed, and distilled over metallic sodium, the hydrocarbons boiled at 28—33°. Their composition was investigated by the hydrogenation method, 1·811 g. requiring 361 c.c. as compared with 637·5 c.c. calculated for pure amylene (see Table IV, No. 6); hence there were 56·7% of amylene and 43·3% of *iso*pentane. Examination of the three sections of the curve (Fig. 3, Curve 3) as before leads to the results given in Tables I and II.

In the foregoing, we have assumed that the first section of Curves Nos. 2 and 3 (Fig. 3) belongs to *iso*propylethylene, and the last to trimethylethylene. This conclusion is based on the rule given in Part I (*loc. cit.*), which may be stated thus: If a mixture of ethylenic derivatives of different degrees of substitution is hydrogenated, the

* The calculation is as follows: 100 Mols. of isoprene require 50 mols. of hydrogen for 25% hydrogenation; if x mols. of amylene and y of *iso*pentane have been formed, we have $x + 2y = 50$, and $x : y = 59 : 41$; hence $x = 21$, $y = 14·5$, and isoprene (by difference) = 64·5%.

monosubstituted ethylene is hydrogenated first, then follow in succession the di-substituted, the tri-substituted, and finally the tetra-substituted derivative. In order to confirm this we made two experiments in which the reaction product was further hydrogen-



ated after admixture with (*a*) *iso*propylethylene and (*b*) trimethylethylene.

(*a*) The weight of the product examined was 1·8053 g., requiring 351·5 c.c. of hydrogen (at 20° and 760 mm.) on the assumption that it contained 56·7% of amylenes (see Table I). The weight of *iso*propylethylene was 0·5465 g., which required 187 c.c. of hydrogen. The corresponding curve is given in Fig. 4 (1).

(*b*) The weight of the product was 1·6931 g., which requires 326 c.c. of hydrogen (at 19° and 765 mm.) on the basis of 56·7% of amylenes. The weight of trimethylethylene was 0·4219 g., which required 148 c.c. of hydrogen. The curve is shown in Fig. 4 (2).

In Table III are shown (1) the amounts of hydrogen required in the various stages as calculated from the weight taken, according to Table I; (2) *the amounts actually consumed in the two* experiments.

TABLE III.

C.c. of hydrogen absorbed in the sections of the curve by hydrogenation in mixture with :

	(*a*) *iso*Propylethylene.		(*b*) Trimethylethylene.	
	Calc.	Found.	Calc.	Found.
Section 1	105 + 187	290	98	100
,, 2	116	125	107	114
,, 3	130	134	121 + 148	265
Total	351 + 187 (538)	549	326 + 148 (474)	479

(*a*) It is evident from the table and Curve 1 that the second and third sections of the curve *remained practically unchanged in size*. Hence, *all the* iso*propylethylene was hydrogenated in the first section*.

(*b*) From the table and Curve 2 it is similarly clear that *the third section of the curve pertains to trimethylethylene*.

The middle section therefore relates to *as*-methylethylethylene.

70% *Hydrogenation*.—In the foregoing cases it has been necessary to extract the unchanged isoprene before examining the mixture of amylenes. In this case, however, all the isoprene has become hydrogenated, and the curves after the 70% stage (" critical point ") refer solely to the hydrogenation of the amylenes which have been accumulating and have not already been reduced to *iso*pentane.

For the addition of the remaining 30% of hydrogen we have three well-defined sections of the curve. The amounts of hydrogen corresponding to each of these sections have already been given (p. 828), and the amonnt of the particular amylene corresponding to each section is obtained by doubling the percentage of hydrogen absorbed over that section. The composition thus calculated is given in the third part of Table II.

General Survey of the Hydrogenation of Isoprene.

The results obtained for 25%, 50%, and 70% hydrogenation of isoprene are given in Table II, and are used for plotting the diagram in Fig. 7.

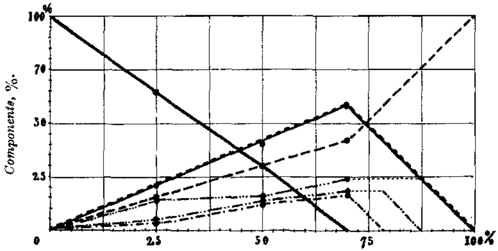
Nearly all the experimental points of the isoprene curve lie on the straight line which joins the terminal point of the axis of ordin-

Table IV.

Numerical data for isoprene hydrogenated totally, partially, and in admixture with monoethylenic derivatives.

Expt. No.	Material.	Weight (g.).	C.c. of H_2 calc.	C.c. of H_2 obs.	Temp.	Press. (mm.).	Pt (g.).	Alcohol (c.c.).	Bath temp.	Curve No.
1	$C_5H_8 + 2H_2$	4·2390	2910	2850	11°	760	0·25	35	10·5°	Fig. 2
2	$C_5H_8 + 2H_2$	0·875	530	525	15	760	0·2	20	13·75	,, 3 (1)
3	$C_5H_8 + \frac{1}{2}H_2$	12·011	2110	2110	16	755	0·2	35	0	
4	$C_5H_8 + H_2$	14·90	5178	5178	17	765	0·2	35	15	
5	$C_5H_8 + \frac{1}{2}H_2$, freed from C_5H_8	0·85	293	173	18	758	0·1	35	0	,, 3 (2)
6	$C_5H_8 + H_2$, freed from C_5H_8	1·811	637·5	361	20	742	0·3	15	17·75	,, 3 (3)
7	Isoprene + *iso*Propylethylene	0·6920 0·8900	473 295	758·5	14	770	0·2	15	12·25	,, 6 (1)
8	Isoprene + Camphene	0·6310 1·3200	448 200	637	17	750	0·2	15	15·5	,, 5 (1)
9	Isoprene + Trimethylethylene	0·8543 0·4780	594 163	755	16	755	0·2	15	0	,, 6 (2)
10	Isoprene + *Tetramethylethylene*	0·4570 *0·2896*	324 *83*	400	17	748	0·2	15	16·25	,, 5 (2)

Fig. 7.



Absorbed hydrogen, %.

Isoprene. — isoPentane. — Total amylenes. — isoPropylethylene. — as-Methylethylethylene. — Trimethylethylene.

● ● Quantities found experimentally.

ates (100%) with the critical point lying on the axis of abscissæ (70%). This means that the reduction of isoprene proceeds proportionally to the amount of the consumed hydrogen until it is entirely reduced.

The curves showing the total amylenes and the *iso*pentane are straight lines up to the critical point, the experimental points lying on straight lines passing through the origin. This attests to the important fact that the accumulation, not only of amylenes, but also of *iso*pentane is going on from the very beginning of the process. The accumulation of these two components is strictly proportional to the amount of the hydrogen consumed up to the critical point.

At this point both curves show a break, the amount of amylenes beginning to decrease towards zero, and that of *iso*pentane increasing to 100%.

The diagram does not answer the important question as to the way in which *iso*pentane is formed. During the second stage of the process, it is obvious that *iso*pentane is formed from the amylenes accumulated before the critical point, but the origin of that formed in the first phase of the process is still unknown. Two possibilities are open:

(1) *iso*Pentane is formed from the amylenes resulting from the addition of 1 mol. of hydrogen to the isoprene. In this case we must assume that it is formed neither from *as*-methylethylethylene nor from trimethylethylene, for the hydrogenation of these two amylenes in presence of *iso*propylethylene is improbable, because the last is the most readily hydrogenated of the three. This is wholly confirmed by the experimental data below. The addition to isoprene of an unsymmetrical disubstituted ethylene or of a trimethylethylene does not displace the critical point, and therefore does not change the amount of fully saturated molecules formed before the critical point is reached.

The partial formation of *iso*pentane from *iso*propylethylene is, however, a possibility. As may be seen from Curve 1, Fig. 6, the *iso*propylethylene added to the isoprene is hydrogenated, as it should be, in the second part of the curve, but the position of the critical point is too indistinct to preclude a partial hydrogenation of the *iso*propylethylene before the critical point.

(2) *iso*Pentane is formed directly from isoprene by addition of 2 mols. of hydrogen either simultaneously or in such rapid succession as to appear to be so. In this case we should have a process analogous to that taking place in the hydrogenation of benzene.

We cannot find any objection to the second hypothesis, but we cannot yet prove it, and the question must be regarded as still unsolved.

We have now to account for the relative quantities of the individual amylenes formed at the hydrogenation.

As shown by the diagram, the curves for the different amylenes depart considerably from straight lines. This is unexpected, for the sum of the three amylenes is expressed by a remarkably regular straight line. This deviation is due to the fact that in the mixture of amylenes the amount of trimethylethylene is greater than is necessary to make the lines of all three amylenes straight. This, in turn, may be due to the isomerisation of two of the amylenes into trimethylethylene. Most probably this secondary process is caused by the action of sulphur dioxide during the elimination of

isoprene from the mixture of the hydrocarbons, for we have noticed that the excess of trimethylethylene was more pronounced the longer the mixture of hydrocarbons had been kept in contact with sulphur dioxide.

Isomerisation of Amylenes by Action of Sulphur Dioxide.—A direct test has demonstrated this isomerisation: We prepared a mixture of amylenes by the decomposition of amyl alcohol (from fusel oil) by aluminium oxide at 400°. A portion was hydrogenated, and the proportion of trimethylethylene in the mixture was found, from the extent of the sections of the hydrogenation curve, to be 27%. Another portion of the mixture was saturated with sulphur dioxide at 0°, sealed, and heated at 100° for 3 days, in order to accelerate the process; it was then freed from sulphur dioxide by washing, distilled over metallic sodium, and hydrogenated, the proportion of trimethylethylene being then 41%, as determined from the curve.

There is therefore some uncertainty as to the original normal composition of the amylenes obtained as a result of the hydrogenation of isoprene. We must consider it to be the composition of the amylenes at the critical point (70% hydrogenation) as shown in the last column of Table II, for in this case the amylenes were not treated with sulphur dioxide. The composition of the amylenes obtained from isoprene hydrogenated up to 25% and 50% must, however, be considered as more or less altered by the action of sulphur dioxide.

Hydrogenation of Isoprene Mixed with Standard Ethylenic Derivatives of Different Degrees of Substitution.

When considering the process as a whole, the following questions arise: (1) How does the addition of different monoethylenic derivatives affect the general type of the isoprene curve and the position of the critical point? (2) How is *iso*pentane formed from the products of hydrogenation?

In order to throw light on these questions we have examined a set of isoprene mixtures with ethylenic derivatives of different degrees of substitution. The numerical data relating to these mixtures are given in Tables IV and V. In Table V are shown: (*a*) the amounts of hydrogen calculated according to the scheme on p. 828 for the four sections of the isoprene hydrogenation curve, (*b*) the amounts of hydrogen that were actually absorbed in these sections in the hydrogenation of isoprene in the various mixtures.

When examining Tables IV and V and the corresponding curves, one must note the following circumstances: The added standard

TABLE V.

C.c. of hydrogen absorbed in the sections of the isoprene curve when hydrogenated in admixture with :

	*iso*Propyl-ethylene.		Camphene.		Trimethyl-ethylene.		Tetramethyl-ethylene.	
	Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.
Section 1	331	328	313	305	416	415·5	228	224
,, 2	38+295	327	41	46	53·5	56·5	27	28
,, 3	41	46	40+200	240	59·5	63	29	28
,, 4	62	59	54	46	65+163	220	40	42
,, 5	—	—	—	—	—	—	0+83	78
Total	472+295	760	448+200	637	594+163	755	324+83	400
	767		648		757		407	

ethylenic derivatives are generally hydrogenated after the critical point in the place determined by the degree of substitution of the given ethylene. Thus the *iso*propylethylene added is hydrogenated in the second section of the curve (Fig. 6, No. 1); camphene in the *third (Fig. 5, No. 1); trimethylethylene in the fourth (Fig. 6, No. 2)*; * *and tetramethylethylene is hydrogenated when all isoprene* is consumed (Fig. 5, No. 2).* The critical point retains its position and is clearly defined in every case except that concerning *iso*-propylethylene. This circumstance allows us to assume that a monosubstituted ethylene can be partially hydrogenated simultaneously with isoprene.

Summary.

(1) In the catalytic hydrogenation of conjugated systems, the process may be of four types :

Type I. In the first phase the addition of hydrogen is directed exclusively into the 1 : 4-position. In the second phase, which proceeds at a different (lesser or higher) rate, 2 : 3-addition occurs.

Type II. In the first phase the addition of hydrogen takes place primarily in all the possible directions (1 : 2, 3 : 4, and 1 : 4), and subsequently until a fully saturated compound is formed. All these reactions proceed simultaneously. The first phase ends with the consumption of the conjugated system at the " critical point of hydrogenation." For the several substances investigated, the critical point corresponds to 68—77% of hydrogen absorbed. In the second phase are hydrogenated those monoethylenic compounds which were formed in the first phase.

Type III. One mol. of a conjugated system absorbs simultaneously 2 mols. of hydrogen, giving a saturated compound directly.

* A dash, marked 100%, on these curves indicates the point where isoprene is consumed and hydrogenation of the admixed substance begins.

Type IV. The addition of hydrogen is directed exclusively into the 1 : 2- and 3 : 4-positions. The double linkages of the conjugated system are hydrogenated independently.

(2) The process of hydrogenation of isoprene belongs to Type II. The first phase, which proceeds at a constant rate, embraces several processes—the addition of 1 mol. of hydrogen in the 1 : 2-, 3 : 4-, and 1 : 4-positions—which lead to the formation of three amylenes, *viz.*, *iso*propylethylene, *as*-methylethylethylene, and trimethylethylene. At the same time some *iso*pentane is formed.

The first phase ends at the "critical point," corresponding to the addition of 70—71% of hydrogen necessary for complete hydrogenation; at this point the whole of the isoprene has been consumed.

In the second phase the accumulated amylenes are consecutively hydrogenated: first the *iso*propylethylene, then the *as*-methylethylethylene, and finally the trimethylethylene.

(3) The hydrogenation curve of isoprene is horizontal in its first phase, but turns upwards at the critical point, denoting an increase in the rate.

In the second phase the curve shows three more or less horizontal sections corresponding to the three amylenes mentioned in (2).

(4) In the hydrogenation of isoprene in admixture with ethylenic compounds, the critical point retains its position.

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CXIV.—*Equilibrium in the Binary Systems: Ethylenediamine–Phenols.*

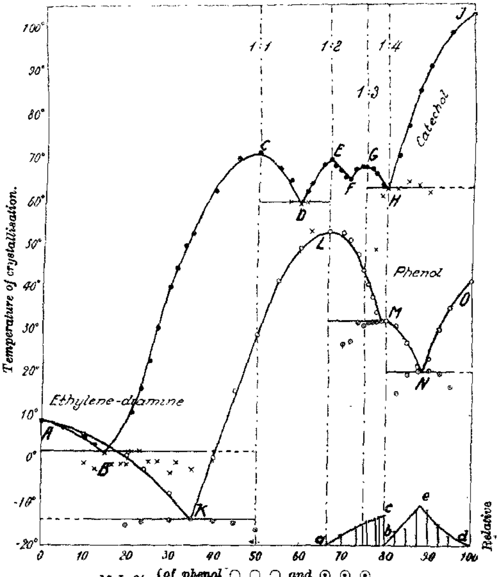
By NIKOLAI ANTONOVICH PUSHIN and LJUDEVIT SLADOVICH.

EQUILIBRIUM diagrams of mixtures of ethylenediamine and phenols have not hitherto been studied, but the thermal analysis of five such systems is now described. For every mixture the following have been determined: (1) the temperature of complete melting of the crystallised mixture; (2) the complete cooling curve; (3) the duration of the eutectic crystallisation.

In the tables, the column headed I under "Temperature" denotes the temperature of first crystallisation (but complete melting in the case of guaiacol), and that headed II refers to the definite (or eutectic) crystallisation. The column headed "Time" shows the duration (in minutes) of the definite crystallisation of 1 g. of substance.

Ethylenediamine-Phenol.—The equilibrium diagram (Fig. 1) is composed of four branches and is characterised by two eutectic points, one open maximum at 66·6 mol. % of phenol, and one transition point at the concentration of 80 mol. % of phenol. It therefore follows that the open maximum corresponds to the form-

FIG. 1.



ation of a definite *compound*, $C_2H_4(NH_2)_2,2C_6H_5\cdot OH$, melting a 53·5°.

For the determination of the composition of the other compound the time of duration of crystallisation at the transition point (31·6° was studied (triangle *abc*). The maximum was found at 80 mol. % of phenol. Hence the *compound* is $C_2H_4(NH_2)_2,4C_6H_5\cdot OH$. Th

TABLE I.

Ethylenediamine–Phenol.

Phenol, mol. %.	Temperature, I.	Temperature, II.	Time.	Phenol, mol. %.	Temperature, I.	Temperature, II.	Time.
0	8·7°		—	73·5	+47·1°	+31·4°	1·4
10	+ 5·6°	—	—	75	+43·5	+30·9	1·5
20	+ 0·6	−15·3°	—	76	+40·2	+31·4	1·7
23·8	− 2·4	−14·6	—	77	+37·2	+31·5	—
30	− 8·0	−14·2	—	78	+33·8	+31·6	1·9
35	−14·0		—	79	+31·8	—	2·0
40	+ 0·1	−14·4	—	80	+31·8	—	2·1
45	+15·5	−14·8	—	82·5	+30·0	+15	1·0
50	+28·6	−16·2	—	85	+26·8	+19·6	1·2
55	+41·2	—	—	87·5	+21·3	+20·1	2·5
60	+48·9	—	—	90	+23	+20·2	2·3
66·6	+52·8	—	—	92·5	+29·9	+19·6	1·5
70	+52·3	+26·5	0·8	95	+34·6	+16·5	0·7
71·5	+50·6	+27	—	100	+40·8°		—

point which corresponds to this compound in the diagram is congruent with the transition point within the limits of the experimental error.

The two eutectic points correspond to (*a*) 35 mol. % of phenol and −14°; (*b*) 88·5 mol. % of phenol and 20·2°. Triangle *bed* shows the time of crystallisation of the mixture at this second eutectic temperature.

TABLE II.

Ethyleuediamine–*o*-Cresol.

o-Cresol, mol. %.	Temperature, I.	Temperature, II.	Time.	*o*-Cresol, mol. %.	Temperature, I.	Temperature, II.	Time.
0	+8·7°		—	50	+29°	—	—
10	4·5°	—	—	55	+37·8	—	—
15	0	−19·4°	1·0	60	+43·8	—	—
20	− 2	—	—	65	+47	—	—
25	− 8·5	−18·2	2·1	66·6	+47·2	—	—
30	−12·7	—	—	70	+45·1	—	—
32·5	−17·2		2·9	75	+37·6	+6·1°	0·8
37·5	− 2	−17·8	2·1	80	+22·9	+8	1·4
40	+ 5·2	—	—	85	—	+8·5	1·0
42·5	+ 9·7	−18·4	1·3	90	+19	+6·6	1·0
45	+16·3	—	—	100	+29·5°		—

Ethylenediamine–o-Cresol.—The equilibrium diagram (Fig. 2) is characterised by one open maximum at the concentration of 66·6 mol. % *o*-cresol, and by two eutectic points: one corresponds to 32·5 mol. % of *o*-cresol and −17°, and the other to 85 mol. % and +8·5°. The maximum shows the formation of a definite *compound*, $C_2H_4(NH_2)_2,2C_7H_7 \cdot OH$, which melts at 48°.

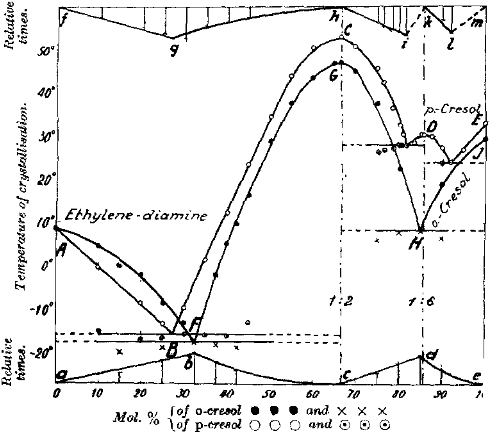
Triangles *abc* and *cde* show the time of crystallisation of the mixtures at the corresponding temperatures and prove the position of the eutectic points on the diagram.

TABLE III.

Ethylenediamine–*p*-Cresol.

p-Cresol, mol. %.	*Temperature,* I.	II.	Time.	*p*-Cresol, mol. %.	*Temperature,* I.	II.	Time.
0	8·7°		—	76·5	+42·6°	+27°	0·9
10	−0·3°	−14·7°	1·0	78·5	+36·6	+27·2	1·0
20	−8·5	−16·6	1·9	80	+32·5	+28·2	1·1
25	−13	−16·4	2·5	80·5	+30·6	+28·1	—
30	−9·5	−15·6	2·9	81·5	—	+28·0	1·3
35	+1·4	−15·6	1·7	83·5	+29·7	—	—
40	+12·2	−15·7	1·4	85	+30·3	—	—
45	+23·5	−13	1·0	85·7	+30·1	—	—
50	+34·5	—	—	87·5	+29·9	—	—
55	+44	—	—	90	+27·4	+23·9	0·6
60	+50·6	—	—	92	—	+24·0	1·2
66·6	+53	—	—	95	+27	—	—
70	+51	—	—	100	+33°		—
75	+45·8	+26·7	0·7				

FIG. 2.



Ethylenediamine–p-*Cresol*.—The equilibrium diagram (Fig. 2) composed of four parts and is characterised by three eutectic poir and two open maxima, one of which lies at 66·6 mol. % and t other at 85·7 mol. % of *p*-cresol. The first maximum shows t formation of the *compound* $C_2H_4(NH_2)_2,2C_7H_7{\cdot}OH$, and the seco

of the *compound* $C_2H_4(NH_2)_2,6C_7H_7{\cdot}OH$. The former compound melts at 54° and the latter at 31°. Between the two maxima lies the eutectic point, which corresponds to 82 mol. % of *p*-cresol and 28·2°. The other two eutectics represent (1) 27 mol. % of *p*-cresol and −13°; (2) 92 mol. % of *p*-cresol and +24°.

Triangles *fgh*, *hik*, and *klm* show the duration of crystallisation at the corresponding eutectic temperatures.

TABLE IV.

Ethylenediamine–Pyrocatechol.

Temp. of crystallisation for 0 mol. % of pyrocatechol, 8·7°; for 100 mol. %, 102·7°.

Pyro-catechol, mol. %.	Temperature, I.	Temperature, II.	Pyro-catechol, mol. %.	Temperature, I.	Temperature, II.	Pyro-catechol, mol. %.	Temperature, I.	Temperature, II.
5	7·2°	—	35	52·2°	− 2·7°	71	64·8°	—
10	5	−1·1°	40	62	—	72·5	66·8	—
12·5	3·2	−2·4	45	69·5	—	74	67·6	—
15	—	+1	50	70·7	—	75	67·6	—
16·5	—	−1·4	55	67·3	+53	76·5	67	—
18·5	—	−1·3	57·5	64·5	+59·7	77·5	66	+48·3°
20	—	−1·4	60	—	+59	79	63·4	+60·8
21	10·6	+1·5	61·5	62	+59·6	80	—	+62·5
23	16	+1·6	62·5	63·8	+52·9	82·5	70	+62·4
25	22·5	−1	65	68	—	85	77	+64
27	30	−0·7	66·6	69·2	—	87·5	85	+63·2
30	39·6	−3·6	67·5	67·7	—	90	90·5	+61·8
31·5	44·2	−1	69	66·8	—	95	98·2	—
33·3	49·5	—	70	65·2	—			

Ethylenediamine–Pyrocatechol.—The equilibrium diagram (Fig. 1) consists of five parts. Three open maxima are clearly indicated. One corresponds to 50 mol. % of pyrocatechol, *i.e.*, to a *compound* $C_2H_4(NH_2)_2,C_6H_4(OH)_2$, which melts at 73°. The second lies at 66·6 mol. % of pyrocatechol and corresponds to a *compound*

$$C_2H_4(NH_2)_2,2C_6H_4(OH)_2,$$

melting at 71°; and the third to 75 mol. % of pyrocatechol, $C_2H_4(NH_2)_2,3C_6H_4(OH)_2$; this *compound* melts at 69·2°.

Three of the eutectic points are clearly indicated: (*a*) at 15 mol. % of pyrocatechol and 2°; (*b*) at 60 mol. % and 60°; (*c*) at 80 mol. % and 64°. The fourth, *viz.*, that between

$$C_2H_4(NH_2)_2,2C_6H_4(OH)_2 \text{ and } C_2H_4(NH_2)_2,3C_6H_4(OH)_2,$$

could not be accurately determined, and the cooling curves gave indications of the formation of solid solutions between these two compounds.

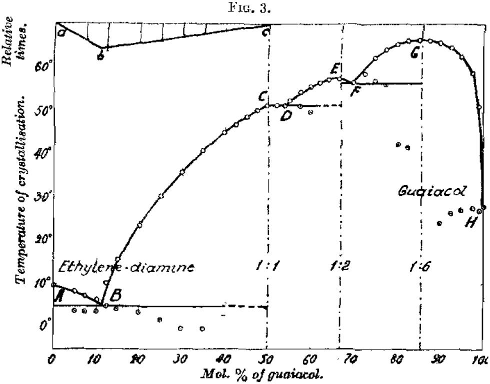
Ethylenediamine–Guaiacol.—This system resembles the preceding, as might be expected in view of the relation between guaiacol and pyrocatechol. The diagram (Fig. 3) consists of four parts. It looks as if ethylenediamine is not soluble in guaiacol, for the curve

TABLE V.

Ethylenediamine–Guaiacol.

Guaiacol, mol. %.	Temperature, I.	Temperature, II.	Time.	Guaiacol, mol. %.	Temperature, I.	Temperature, II.
0	9·4°	—	—	60	55·8°	+50°
5	8	+ 3·5°	–	62	56·9	—
7·5	7	+ 3·2	1·1	64	57·5	—
10	6	+ 3·5	—	66·6	57·5	—
12·5	10	+ 4·8	1·9	70	56·8	—
15	15·3	+ 4	—	72·5	59	—
20	23·2	+ 3·2	1·3	75	62·4	+57·2
25	30·2	+ 1·5	1·2	77·5	64·5	+56·7
30	35·8	− 0·4	0·8	80	65·4	+42·6
35	40·7	− 0·5	0·7	82·5	66·3	+41·7
40	45	—	—	85	66·5	—
42·5	46·8	—	—	87·5	66·5	—
45	48·8	—	—	90	65·8	+24
47·5	50·1	—	—	92·5	64·8	+26·5
50	51·5	—	—	95	62·5	+27
52	51·5	—	—	97·5	59	+27·5
54	51·5	—	—	99	51·2	+27
55	52·2	—	—	100	—	+28°
57·5	54·2	+ 51·3	—			

FIG. 3.



ascends steeply from pure guaiacol, forming an open maximum a 85 mol. % of guaiacol, corresponding to a *compound*

$$C_2H_4(NH_2)_2,6C_6H_4(O{\cdot}CH_3)(OH).$$

This is the most characteristic of the three compounds formed b these components, and melts at 66·5°. If one bears in mind the

there is but one hydroxyl group in guaiacol, whilst there are two in pyrocatechol, the above-mentioned compound is analogous to $C_2H_4(NH_2)_2,3C_6H_4(OH)_2$. With pure guaiacol this compound forms only mechanical mixtures, since in the interval from 85—100 mol. % of guaiacol the temperature of crystallisation of the latter is clearly noticeable.

The second maximum in the diagram corresponds to 66·6 mol. % of guaiacol, and therefore to $C_2H_4(NH_2)_2,2C_6H_4(O{\cdot}CH_3)(OH)$, which melts at 57·5°. This *compound* is analogous to

$$C_2H_4(NH_2)_2,C_6H_4(OH)_2.$$

The third maximum lies at 50 mol. % of guaiacol and shows the formation of a *compound*, $C_2H_4(NH_2)_2,C_6H_4(O{\cdot}CH_3)(OH)$, m. p. 51·5°. The eutectic point between this compound and pure ethylenediamine corresponds to 11 mol. % of guaiacol and 5°.

The triangle *abc* shows the time of crystallisation at this eutectic temperature. Judging by the fact that the eutectic crystallisation is clearly noticeable in the interval of 0—50 mol. % of guaiacol, pure ethylenediamine and its equimolecular compound with guaiacol do not form solid solutions.

Summary.

Equilibrium has been determined in five binary systems composed of ethylenediamine on the one hand and phenol, *o*- and *p*-cresol, pyrocatechol, and guaiacol on the other. The existence has been demonstrated of the following definite compounds, which all melt without decomposition :

$C_2H_4(NH_2)_2,2C_6H_5{\cdot}OH$	$C_2H_4(NH_2)_2,2o\text{-}C_6H_4Me{\cdot}OH$	$C_2H_4(NH_2)_2,o\text{-}C_6H_4(OMe){\cdot}OH$
$C_2H_4(NH_2)_2,4C_6H_5{\cdot}OH$	$C_2H_4(NH_2)_2,o\text{-}C_6H_4(OH)_2$	$C_2H_4(NH_2)_2,2o\text{-}C_6H_4(OMe){\cdot}OH$
$C_2H_4(NH_2)_2,2p\text{-}C_6H_4Me{\cdot}OH$	$C_2H_4(NH_2)_2,2o\text{-}C_6H_4(OH)_2$	$C_2H_4(NH_2)_2,6o\text{-}C_6H_4(OMe){\cdot}OH$
$C_2H_4(NH_2)_2,6p\text{-}C_6H_4Me{\cdot}OH$	$C_2H_4(NH_2)_2,3o\text{-}C_6H_4(OH)_2$	

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CXV.—*Differential Potentiometric Titration. Part I. Simple Method (Method I).*

By BERNARD CAVANAGH.

THE potential of a suitable electrode dipping into a titrated solution has been used for the detection of the end-point according to two distinct principles. The more obvious principle, that a particular *value* of the potential marks the end-point, came into use comparatively recently with the methods of Pinkhof, Treadwell, and Müller (Müller, " Electrometrische Massanalyse," 4te Aufl., Berlin; see also Cavanagh, J., 1927, 2207). In earlier methods the end-

point was detected by a *rapid change* in the potential, or, more precisely, by a maximum in the value of $\Delta E/\Delta M$ (where E is the potential, and M the amount of reagent used). This "differential" indication is intrinsically less sensitive than the other, but has the advantage at present of wider application. Moreover, in some of the cases where the more convenient "absolute" principle is applicable, the exact determination of the particular potential which marks the end-point depends ultimately on the use of the differential principle.

The methods described in this and the following paper depend upon a broader conception of the differential principle and, while retaining the advantage of wide applicability, appear to be an improvement upon the usual methods, both in convenience and in precision. Instead of the customary process of making a large number of small additions of reagent with corresponding potential measurements in order to detect the maximum value of $\Delta E/\Delta M$, it has been found possible to determine the result of the titration with higher precision from two or three measurements of the potential, corresponding to one or two *large* additions of the reagent, without necessarily finishing the titration in the ordinary sense. Indeed the simple method now described depends on the assumption that the added reagent reacts completely with the titrated solution, which implies that the end-point is not quite reached. This sets a limit to the absolute precision attainable by this method with given electrodes. For example, in the titration of a chloride by means of silver nitrate, if the electrodes are trustworthy as regards constancy to $\pm$ 0·25 millivolt, so that the change of potential is defined to $\pm$ 0·5 millivolt, the maximum absolute precision is about one-seventh of the solubility of silver chloride, *i.e.*, about $\pm$ 0·2% in the titration of an $N/1000$ solution. About five times this degree of absolute precision is obtainable, with electrodes of the same constancy, by the use of methods II and III which take account of the incompleteness of the reaction in the neighbourhood of the end-point (see Part II, following paper).

1. *Principle of Method I.*—The potential of a reversible electrode dipping into a solution of the corresponding (univalent) ion, concentration c, is given by the formula

$$E = \text{constant} + RT/F.\log c\gamma \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the activity coefficient of the ion. Suppose this ion is to be titrated by means of a standard reagent of normality n, and that the solution is chemically equivalent to M_0 c.c. of the reagent, so that the object of the titration is to determine M_0. If the volume

of the solution is V_0 c.c., the concentration c is equal to nM_0/V_0, and the initial potential of the electrode is

$$E_0 = \text{constant} + RT/F . \log nM_0\gamma_0/V_0 \quad . \quad . \quad . \quad (2)$$

Suppose now that any quantity, m c.c. (less than M_0) of the reagent is added to the solution, reacting completely. The solution is now equivalent to $(M_0 - m)$ c.c., and the volume is increased to $(V_0 + m)$ c.c. The potential of the electrode will therefore be

$$E = \text{constant} + RT/F . \log nM\gamma/V \quad . \quad . \quad . \quad (3)$$

where $M = (M_0 - m)$, $V = (V_0 + m)$, and γ is the activity coefficient under the changed conditions. The potential *change*, ε, due to the addition of m c.c. of reagent is therefore

$$\varepsilon = RT/F . \log nM_0\gamma_0/V_0 - RT/F . \log nM\gamma/V \quad . \quad . \quad (4)$$

$$= RT/F . \log M_0\gamma_0/V_0 - RT/F . \log M\gamma/V \quad . \quad . \quad (5)$$

As a first approximation we can put $\gamma_0 = \gamma$, and if m is assumed to be negligibly small in comparison with V_0, we can put $V = V_0$; then

$$\varepsilon = RT/F . \log M_0/M = RT/F . \log (1 + m/M) . \quad . \quad (6)$$

Thus, at constant temperature, ε is a function of m/M; and conversely, *the ratio* M/m *is a function of* ε; explicitly (see Table I)

$$M/m = f(\varepsilon) = \tfrac{1}{2}(\coth F\varepsilon/2RT - 1) \quad . \quad . \quad . \quad (7)$$

Thus the measurement of a single potential change (ε), produced by the addition of the arbitrary quantity of reagent (m c.c.) suffices with the aid of Table I to determine M, and therefore M_0, the result of the titration.

2. *Correction for the Changing Volume of the Solution, and for Change in the Activity Coefficient.*—The foregoing approximations can be dispensed with, however, for ε (equation 5) can be divided into three additive parts,

$$\varepsilon = \varepsilon_m + \varepsilon_v - \varepsilon_\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$\varepsilon_m = RT/F . \log M_0/M = RT/F . \log (1 + m/M) \quad . \quad . \quad (9)$$

$$\varepsilon_v = RT/F . \log V/V_0 = RT/F . \log (1 + m/V_0) \quad . \quad . \quad (10)$$

$$\varepsilon_\gamma = RT/F . \log \gamma/\gamma_0 = RT/F . \log [1 + (\gamma - \gamma_0)/\gamma_0] \quad . \quad (11)$$

and comparison with equations (5) and (6) shows that

$$M/m = f(\varepsilon_m) = f(\varepsilon - \varepsilon_v + \varepsilon_\gamma) \quad . \quad . \quad . \quad (12)$$

$$V_0/m = f(\varepsilon_v) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\gamma_0/(\gamma - \gamma_0) = f(\varepsilon_\gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Thus M/m can be obtained from ε_m exactly as (in neglecting m and $\gamma - \gamma_0$) it was obtained from ε, and the "corrections," ε_v and ε_γ,

can be estimated by using Table I in the inverse way—as in finding an antilogarithm from a table of logarithms. (But see also section 11 and 12.)

The activity coefficient of an ion in a mixed salt solution depends to a first approximation, on the "*ionic strength*" of the whole solution (see Lewis and Randall, "Thermodynamics," McGraw-Hill New York), which may be defined as "half the sum of the equivalent concentrations of all the ions present multiplied respectively by their valencies." In the course of a titration, one ion is gradually substituted for another in the titrated solution, while at the same time the volume of the solution is increased. When the "exchanged" ions are of the same valency (as in the titration of halides by means of silver nitrate, or of acids by sodium hydroxide), the ionic strength changes only on account of the increasing volume, to which it is inversely proportional, and even if the volume is doubled the relative change in γ is only 2—4%. The corresponding value of ε_γ is therefore less than 1 millivolt—generally much less. When, as in titration with barium hydroxide, a bivalent ion is being substituted for a univalent, the effect of the increasing volume upon the ionic strength of the solution is partly or wholly counterbalanced, and ε_γ is still smaller. Thus, ε_γ is almost always negligible, so that (12) may then be abbreviated to

$$M/m = f(\varepsilon_m) = f(\varepsilon - \varepsilon_v) \quad . \quad . \quad . \quad . \quad (15)$$

The dilution correction, ε_v, on the other hand, may be quite large; *e.g.*, if the added volume of reagent is equal to the initial volume of the titrated solution, $V_0/m = 1$, and ε_v (see Table I) = 17·3 millivolts.

3. *The precision of the determination* is limited ultimately by the inherent variability of the electrodes which appears (multiplied by 2) in ε as an uncertainty which is "absolute," *i.e.*, independent of the magnitude of ε. The consequent absolute uncertainty in the determination of M_0 is therefore found by differentiating M partially with respect to ε, ε_v and m being treated as constants thus

$$-\partial M_0/\partial\varepsilon = FM_0M/RTm = 0{\cdot}04M_0M/m \text{ (at } 17^\circ) \quad (16)$$

and the *relative* uncertainty per millivolt of uncertainty in ε

$$-(\partial M_0/\partial\varepsilon)/M_0 = 0{\cdot}04(M_0/m - 1) \; . \quad . \quad . \quad (17)$$

Thus the relative uncertainty in M_0 corresponding to an uncertainty of $\pm$ 0·5 millivolt in ε is roughly 20% when m is 10% of M_0, 2% when m is 50% of M_0, and 0·2% when m is 90% of M_0.

The importance of having removed the limitation upon the value of m is now plain, for the precision of the result increases rapidly

ith m. *It is still essential, however, that m should be less than* M_0. If the result of the titration (M_0) is approximately known eforehand, m may be made large at once, and a precise result btained from the measurement of a *single potential change*. Otherise the reagent must be added in two or even three stages with orresponding potential measurements, the process being one of uccessive approximation (see examples below).

4. It is not necessary that ε and m should be measured always om the beginning of the titration. Any stage may be taken as the tarting point, for at any stage (so long as the reaction may be egarded as complete), if M' is the volume of reagent still required, nd the volume of the solution is V' c.c., the concentration of the trated ion is nM'/V', the potential of the electrode is

$$E' = \text{constant} + RT/F.\log nM'\gamma'/V' \quad . \quad . \quad (18)$$

nd if ε and m are measured from this stage,

$$\varepsilon = RT/F.\log M'\gamma'/V' - RT/F.\log M\gamma/V \quad . \quad (19)$$

$$= \varepsilon_m + \varepsilon_v - \varepsilon_\gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

here

$$\left.\begin{aligned} M/m &= f(\varepsilon_m) = f(\varepsilon - \varepsilon_v + \varepsilon_\gamma) \\ V'/m &= f(\varepsilon_v) \\ \gamma'/(\gamma - \gamma') &= f(\varepsilon_\gamma) \end{aligned}\right\} \quad . \quad . \quad . \quad (21)$$

r, when ε_γ is negligible,

$$M/m = f(\varepsilon_m) = f(\varepsilon - \varepsilon_v) \quad . \quad . \quad . \quad . \quad (22)$$

hen, instead of (17), a more general expression for the relative ncertainty in the determination of M_0 is obtained, *viz.*,

$$-\frac{1}{M_0}\cdot\frac{\partial M_0}{\partial\varepsilon} = -\frac{1}{M_0}\cdot\frac{\partial M}{\partial\varepsilon} = 0{\cdot}04\,.\,\frac{M'M}{mM_0} = 0{\cdot}04\left(1 + \frac{M}{m}\right)\frac{M}{M_0} \quad (23)$$

$$= 0{\cdot}04[1 + f(\varepsilon_m)]M/M_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

hich shows that precision depends on the smallness of M relative to M_0, and also *up to a point* on the smallness of M/m or $f(\varepsilon_m)$. But hen ε_m is 60 millivolts or more, $f(\varepsilon_m)$ is less than 0·1, and the factor $[1 + f(\varepsilon_m)]$ cannot be much diminished by further increasing ε_m, that precision then depends chiefly on the smallness of M/M_0, hich is independent of the stage from which m is reckoned. On e other hand, the temperature correction (see Section 5) is proortional to ε, and the correction, ε_γ, for variation in the activity efficient increases with m. Hence it is sometimes advantageous to duce the final values of ε and m somewhat by reckoning them om the second, or even from a third, stage in the titration (see xample 1, Section 10).

5. *Temperature Correction.*—Table I (as also Tables II and II*a*) is strictly applicable only at 17°, and the potential change if measured at any other temperature ($t°$) ought to be corrected to 17° by the addition of the small (positive or negative) correction, $(17 - t)\varepsilon/300$, which, however, is often smaller than the experimental uncertainty in ε.

A moderate constancy of temperature is assumed, for, without knowledge of the temperature coefficients of the electrodes, the effect of any slight change of temperature between the measurements of the two potentials E' and E cannot be predicted, and must be included in the experimental uncertainty of ε.

The measurements recorded in Section 10 were obtained without the use of a thermostat.

6. *Applicability of the Method.*—The method as described is applicable to the titration of univalent ions, *e.g.*, $Ag^{\cdot}$, $H^{\cdot}$, Cl', Br', I', OH', etc., to which a corresponding reversible electrode can be found. In the case of a bivalent ion, it would only be necessary to multiply all potentials by 2.

7. *Correction for Adsorption of the Titrated Ion.*—In the case of precipitation titrations, the possible adsorption of the titrated ion by the precipitate has to be considered (compare Part II, Section 1). If at the stage (M, V), the fraction $(1-\theta)$ of the total amount of the ion is adsorbed, the concentration in the solution will be reduced to $nM\theta/V$, and similarly at the earlier stage (M', V'), $(1-\theta')$ being the fraction adsorbed, the concentration will be $nM'\theta'/V'$, so that in the complete expression for ε (equation 8) an additional term, $\varepsilon_\theta = RT/F . \log \theta'/\theta$, will be introduced. For small values of $(1 - \theta)$, $\varepsilon_\theta \approx RT(\theta' - \theta)/F$. If further, as a first approximation, the fraction can be regarded as independent of the concentration of the ion and proportional to the ratio of the amount of precipitate to the volume of solution, so that $(1 - \theta) \propto n(M_0 - M)/V$, then $\varepsilon_\theta \propto nmV_0/VV'$, which means (*a*) that ε_θ will be greater in titrating stronger solutions, and (*b*) that it can be minimised by the procedure of Section 4.

It would be possible to eliminate this source of error almost entirely by filtering off and washing the precipitate with small quantities of water, making the necessary allowance in ε_v for the increased volume of the solution. In the measurements recorded in Section 10, the correction ε_θ, like ε_γ, has been neglected, so that it was probably very small in these cases.

Modification for Oxidation–Reduction Titrations.—The method can be adapted to oxidation–reduction titrations such as the titration of ferrous or titanous ions. In these cases the dilution correction, ε_θ, does not occur, but a correction ε_m. has to be made for change in

the concentration of the oxidised ion. If m' c.c. is the total amount of reagent already added before the further addition of m c.c., and if M c.c. is the unknown amount still required one finds

$$\varepsilon = \varepsilon_m + \varepsilon_{m'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where [compare (21) and (22)]

$$\begin{cases} M/m = f(\varepsilon_m) = f(\varepsilon - \varepsilon_{m'}) & . \quad . \quad (26) \\ m'/m = f(\varepsilon_{m'}) & . \quad . \quad . \quad . \quad . \quad . \quad (27) \end{cases}$$

so that a very similar procedure appears to be applicable. In other cases both ε_r and $\varepsilon_{m'}$ would occur.

9. *The Limit of Precision.*—The method depends on the condition that the reagent added to the solution *reacts completely*, removing from the solution a chemically equivalent quantity of the titrated ion. In the strict sense of course this condition would never be fulfilled, but it holds to a close approximation except in the immediate neighbourhood of the end-point. For example, when silver nitrate is added to a solution of a chloride the residual concentration of silver ion, which remains in solution, thereby failing to remove its equivalent of chloride ion from the solution, is inversely proportional to the chloride-ion concentration, inasmuch as the solubility product ($S^2 = C_{Ag} \cdot C_{Cl}$) is constant. To a first approximation the consequent relative error in the found value of M is C_{Ag}/C_{Cl} or S^2/C^2_{Cl} (*i.e.*, S^2V^2/M^2n^2).

Now with electrodes of the constancy described above, the potential change is defined to within $\pm 0{\cdot}5$ millivolt, and the minimum relative uncertainty in the found value of M is $\pm 0{\cdot}5F/RT$, or $\pm 0{\cdot}02$, which will be exceeded by the error due to the neglect of C_{Ag} unless $C_{Cl} > 7S$ (*i.e.*, $M > 7SV/n$). This sets a limit to the closeness of approach to the end-point, and therefore to the absolute precision (in terms of concentration) attainable by this method, with such electrodes. The minimum absolute uncertainty will be, in fact, rather more than one-seventh of the solubility of silver chloride ($0{\cdot}02 \times 7S$), that is to say, about $\pm 2 \times 10^{-6}$ (*i.e.*, about $\pm 0{\cdot}2\%$ in the titration of $N/1000$-chloride solution with a relatively concentrated reagent).

The considerations of this section apply also to other titrations to which the method is applicable, if the appropriate ionic product is inserted in place of $C_{Ag} \cdot C_{Cl}$, and the limit of absolute precision is estimated accordingly.

For exceptional purposes a somewhat higher order of absolute precision can be obtained with the same electrodes by approaching the end-point more closely, taking into account the incompleteness of the reaction (see Part II).

As a first approximation the correction S^2V^2/M^2n^2 may be subtracted from the found value of M when the latter is less than about $10SV/n$, but the limit $7SV/n$ (about) should not be appreciably overstepped.

10. *Results.*

A few typical titrations by this method are recorded below. The dilute solutions of known relative strength were prepared in the manner described in a previous paper (*loc. cit.*). The same pointer galvanometer was used. A good potentiometer and checked standard cell were actually employed, but it should be observed that since the method depends only on *differences* of potential of the order of 0·1 volt or less, precision better than say, 0·1%, either in the standard cell or in the calibration of the potentiometer, is generally superfluous. The electrodes were silver-halide–quinhydrone pairs, as described in the cited paper, so that the uncertainty of a liquid-junction potential had not to be considered. At the same time the use of these electrodes necessitated the doubling of the dilution correction ε_v, since the potentials of both electrodes were equally affected by the changing volume of the solution. A small measured quantity of the reagent was, in most cases, added *before* the first measurement of the potential (Stage 0), as it was found that the initial potential was more trustworthy if obtained in the presence of a trace of precipitate. In the first example, where the temperature was markedly different from 17° and a rather large value of ε was obtained at Stage III, the advantage of reducing ε, by reckoning ε and m from Stage II, is illustrated (indicated by "III—II"; see also examples 5 and 6). Example 6 illustrates one peculiar advantage of this method, *viz.*, that it is *independent of the immediate neighbourhood of the end-point.* The establishment of a steady and reproducible potential in the case of the iodide electrode is very slow near the end-point, whereas, at a distance from the end-point, measurements can be made quickly and yield an accurate result.

In the examples, col. 2 shows the total number of c.c. of reagent present; col. 3, the volume added after stage 0 (or between the stages indicated); col. 5, the values of $2\varepsilon_v$ (in millivolts) as obtained from Table I; col. 6, the measured potential, E, in millivolts; col. 7, ε, the potential change from stage 0 (or between the stages indicated); col. 8, the difference $\varepsilon - 2\varepsilon_v = \varepsilon_m$; the values in col. 9 are obtained from Table I; col. 10 gives the number of c.c. still required; col. 11, the successive approximations to M_0; and col. 12, the percentage error, Δ.

Example 1. 100 C.c. $N/100$-KCl titrated (at 13°) by $N/100$-$AgNO_3$.

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/1000$.)

$V_0 = 101$.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Stage.	$M_0 - M$.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	1				307·2						
I	11	10	10·1	4·7	299·4	7·8	3·1	7·6	76	87	−12
II	71	70	1·44	26·3	250·5	56·7	30·4	0·421	29·5	100·5	+ 2
III	96	95	1·06	33·1	184·9	122·3	89·2	0·0290	2·75	98·75	+ 0·25
		Correcting to 17°, $\epsilon_{17°}$ =				123·9	90·8	0·0272	2·58	98·58	+ 0·08
II—II	96	25		6·8	$\epsilon_{13°}$ =	65·6	58·8	$0·105_2$	2·63	98·63	+ 0·13
		Correcting to 17°, $\epsilon_{17°}$ =				66·5	59·7	$0·101_1$	2·53	98·53	+ 0·03

Example 2. 100 C.c. $N/400$-KCl titrated (at 16·5°) by $N/100$-$AgNO_3$.

(Actually known to be equivalent to 24·62 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/1000$.)

$V_0 = 101$.

Stage.	$M_0 - M$.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	1				252·8						
I	11	10	10·1	4·7	233·8	19	14·3	1·30	13	24	− 2·5
II	23	22	4·6	9·8	175·5	77·3	67·5	0·072	$1·58_8$	$24·58_5$	− 1·4

Example 3. 1000 C.c. $N/1000$-KCl titrated (at 14·5°) by $N/100$-$AgNO_3$.

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/2500$.)

$V_0 = 1010$.

Stage.	$M_0 - M$.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ
0	10				222·0						
I	40	30	33·7	1·5	210·4	11·6	10·1	2·01	60·3	100·3	+ 1·8
II	85	75	13·5	3·6	172·2	40·8	46·2	0·187	14·0	99·0	+ 0·5
		Correcting to 17°, $\epsilon_{17°}$ =				50·2	46·6	$0·183_5$	13·75	98·75	+ 0·25
Approximate correction for incomplete reaction = $-\frac{S^2V^2}{n^2M} \approx$							−0·1 →		13·65	08·65	+ 0·15

Example 4. 100 C.c. $N/1000$-KCl titrated (at 20°) by $N/1000$-$AgNO_3$.

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/4000$.)

$V_0 = 105$.

Stage.	$M_0 - M$.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	5				250·7						
I	25	20	5·25	8·7	236·3	14·4	5·7	3·9	78	103	+4·5
II	75	70	1·5	25·6	190·4	60·3	34·7	$0·332_6$	23·28	08·28	−0·22
		Correcting to 17°, $\epsilon_{17°}$ =				59·7	34·1	$0·343_5$	24·05	99·05	+ 0·55
Approximate correction for incomplete reaction = $-\frac{S^2V^2}{n^2M} \approx$								−0·2	23·85	98·85	+ 0·35

Example 5. 500 C.c. of $N/5000$-KBr titrated (at 19°) by $N/1000$-$AgNO_3$.

(Actually known to be equivalent to 90·8 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/10,000$.)

V_0 = 500.

Stage.	$M_0 - M$.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	0				340·5						
I	50	50	10	4·7	315·2	25·3	20·6	0·78	39	89	−2
II	80	80	6·25	7·4	279·1	61·4	54·0	0·130$_4$	10·44	90·44	−0·4
III	88	88	5·7	8·1	243·7	96·8	88·7	0·0296$_5$	2·61	90·61	−0·2
		Correcting to 17°, $\epsilon_{17°}$ =				96·2	88·1	0·0304	2·68	90·68	−0·13
III—I	88	38		3·4	$\epsilon_{19°}$ =	71·5	68·1	0·0702	2·67	90·67	−0·14
		Correcting to 17°, $\epsilon_{17°}$ =				71·0	67·6	0·0718	2·73	90·73	−0·08
III—II	88	8	Uncorrected ϵ_m (at 19°) =				34·7	0·333	2·66	90·66	−0·15

Example 6. 1000 C.c. of $N/10,000$-KI titrated (at 19·5°) by $N/1000$-$AgNO_3$.

(Actually known to be equivalent to 111·1 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/20,000$.)

V_0 = 1000.

Stage.	$M_0 - M$.	m.	V_0/m.	$2\epsilon_v$.	E.	ϵ.	ϵ_m.	$f(\epsilon_m)$.	M.	M_0.	Δ.
0	0				440·5						
I	50	50	20	2·4	422·7	17·8	15·4	1·17	58·5	108·5	−2·5
II	100	100	10	4·7	377·5	63·0	58·3	0·107$_4$	10·76	110·76	−0·3
		Correcting to 17°, $\epsilon_{17°}$ =				62·5	57·8	0·110	11·0	111·0	−0·00
II—I	100	50	Uncorrected ϵ_m (at 19·5°) =				42·9	0·219	10·95	110·95	−0·1

Addendum.

11. Although ϵ_v may be obtained from V_0/m or V'/m as explained on p. 846, it is desirable to have a table which reads directly and not inversely; the function derived from equation (10) is more suitable for tabulation in terms of m/V_0 (or m/V') than in terms of V_0/m, and Table II gives ϵ_v in millivolts for values of m/V_0 up to 2·1, *i.e.*, over the range usually required. When, as is often the case, V_0 is a simple number such as 10, 20, 50, the ratio m/V_0 is readily evaluated, and Table II provides the easiest way of "correcting to constant volume" all the measured potentials. Alternatively, Table IIA is more convenient when V (instead of V_0 or V') is a simple number.

12. More generally, the measured potentials may readily be "corrected" to any arbitrarily chosen simple volume by means of Tables II and IIA. For example, if 73·7 c.c. of solution are titrated and 20, 35, 7, and 1·5 c.c. are the successive additions of reagent, the five measured potentials can be "corrected" to 100 c.c. volume as follows, the correction when positive being made in the *same* direction as the change of potential during the titration.

Stage.	Volume, V c.c.	$(100 - V)$.	$\frac{(100 - V)}{100}$.	Corr. (millivolts).	
0	73·7	+26·3	+0·263	+7·6	from Table IIA.
I	93·7	+ 6·3	+0·063	+1·6	
II	128·7	−28·7	−0·287	−6·3	from Table II.
III	135·7	−35·7	−0·357	−7·6	
IV	137·2	−37·2	−0·372	−7·9	

TABLE I.

$$f(\epsilon) = \tfrac{1}{2}(\coth F\epsilon/2RT - 1).$$

ϵ is given in millivolts; $T = 290°$ Abs.

ε.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
0	∞	250	125	83	62	50	41	35·$_9$	30·$_6$	27·$_8$
1	24·$_5$	22·$_3$	20·$_8$	18·$_7$	17·$_8$	16·$_3$	15·$_1$	14·$_1$	13·$_4$	12·$_1$
2	12	11·$_4$	10·$_9$	10·$_4$	9·9$_3$	9·5$_1$	9·1$_8$	8·7$_7$	8·4$_4$	8·1$_3$
3	7·8$_4$	7·5$_9$	7·3$_3$	7·0$_9$	6·8$_8$	6·6$_3$	6·4$_0$	6·2$_7$	6·0$_9$	5·9$_3$
4	5·7$_4$	5·6$_1$	5·4$_7$	5·3$_3$	5·2	5·0$_7$	4·9$_3$	4·8$_4$	4·7$_3$	4·6$_2$
5	4·5$_3$	4·4$_3$	4·3$_3$	4·2$_3$	4·1$_6$	4·0$_6$	3·9$_8$	3·9	3·8$_5$	3·7$_6$
6	3·6$_9$	3·6$_2$	3·5$_5$	3·4$_8$	3·4$_2$	3·3$_7$	3·3$_1$	3·2$_5$	3·2	3·1$_5$
7	3·09$_6$	3·04$_2$	2·99$_5$	2·94$_9$	2·90$_3$	2·85$_8$	2·81$_6$	2·77$_2$	2·73$_2$	2·69$_2$
8	2·65$_2$	2·61$_3$	2·57$_6$	2·54	2·50$_4$	2·46$_9$	2·43$_6$	2·40$_3$	2·37	2·33$_9$
9	2·30$_9$	2·27$_3$	2·24$_8$	2·21$_9$	2·19$_1$	2·16$_3$	2·13$_4$	2·11	2·08$_4$	2·05$_8$
10	2·03$_3$	2·00$_9$	1·98$_5$	1·96$_1$	1·93$_8$	1·91$_6$	1·89$_4$	1·87$_2$	1·85$_1$	1·83
11	1·80$_9$	1·78$_9$	1·76$_9$	1·75	1·73$_1$	1·71$_2$	1·69$_4$	1·77$_6$	1·75$_8$	1·64
12	1·62$_3$	1·60$_6$	1·59	1·57$_3$	1·55$_7$	1·54$_2$	1·52$_8$	1·51$_1$	1·49$_6$	1·48$_1$
13	1·46$_6$	1·45$_2$	1·43$_8$	1·42$_4$	1·41	1·39$_7$	1·38$_3$	1·37	1·35$_7$	1·34$_6$
14	1·33$_7$	1·32	1·30$_8$	1·29$_6$	1·28$_3$	1·27$_2$	1·26$_2$	1·24$_9$	1·23$_8$	1·22$_7$
15	1·21$_6$	1·20$_6$	1·19$_5$	1·18$_3$	1·17$_4$	1·16$_4$	1·15$_4$	1·14$_4$	1·13$_5$	1·12$_5$
16	1·11$_5$	1·10$_6$	1·09$_7$	1·08$_8$	1·07$_9$	1·07	1·06$_1$	1·05$_2$	1·04$_4$	1·03$_5$
17	1·02$_7$	1·01$_9$	1·01	1·00$_2$	0·99$_4$	0·98$_6$	0·97$_9$	0·97$_1$	0·96$_3$	0·95$_6$
18	0·94$_9$	0·94$_1$	0·93$_4$	0·92$_7$	0·92	0·91$_3$	0·90$_6$	0·89$_9$	0·89$_3$	0·88$_6$
19	0·87$_9$	0·87$_3$	0·86$_6$	0·85$_9$	0·85$_3$	0·84$_6$	0·84	0·83$_4$	0·82$_8$	0·82$_2$
20	0·81$_6$	0·81	0·80$_4$	0·79$_8$	0·79$_3$	0·78$_7$	0·78$_2$	0·77$_6$	0·77	0·76$_5$
21	0·76	0·75$_4$	0·74$_9$	0·74$_4$	0·73$_9$	0·73$_4$	0·72$_9$	0·72$_4$	0·71$_9$	0·71$_4$
22	0·70$_9$	0·70$_4$	0·69$_9$	0·69$_4$	0·69	0·68$_5$	0·68$_1$	0·67$_6$	0·67$_1$	0·66$_7$
23	0·66$_3$	0·65$_9$	0·65$_4$	0·65	0·64$_6$	0·64$_1$	0·63$_7$	0·63$_3$	0·62$_9$	0·62$_5$
24	0·620$_6$	0·616$_5$	0·612$_5$	0·608$_5$	0·604$_7$	0·600$_9$	0·597	0·593$_2$	0·589$_6$	0·585$_7$
25	0·582	0·578$_3$	0·574$_7$	0·571$_1$	0·567$_5$	0·564	0·560$_5$	0·557	0·553$_3$	0·550$_1$
26	0·546$_7$	0·543$_8$	0·540	0·536$_7$	0·533$_4$	0·530$_2$	0·526$_9$	0·523$_7$	0·520$_5$	0·517$_4$
27	0·514$_3$	0·511$_1$	0·508$_1$	0·505	0·502	0·499	0·496	0·493	0·490$_1$	0·487$_2$
28	0·484$_3$	0·481$_5$	0·478$_6$	0·475$_8$	0·473	0·470$_3$	0·467$_5$	0·464$_7$	0·462	0·459$_3$
29	0·456$_7$	0·454	0·451$_4$	0·448$_8$	0·447$_3$	0·443$_6$	0·441$_1$	0·438$_6$	0·436	0·433$_6$
30	0·431	0·428$_6$	0·426$_1$	0·423$_7$	0·421$_3$	0·418$_9$	0·416$_6$	0·414$_2$	0·411$_9$	0·409$_6$
31	0·407$_3$	0·405	0·402$_7$	0·400$_5$	0·398$_2$	0·396	0·393$_8$	0·391$_6$	0·389$_4$	0·387$_3$
32	0·285$_1$	0·383	0·380$_9$	0·378$_8$	0·376$_7$	0·374$_7$	0·372$_6$	0·370$_6$	0·368$_5$	0·366$_5$
33	0·364$_5$	0·362$_6$	0·360$_6$	0·358$_6$	0·356$_7$	0·354$_8$	0·352$_8$	0·350$_9$	0·349	0·347$_2$
34	0·345$_3$	0·343$_5$	0·341$_6$	0·339$_8$	0·338	0·336$_2$	0·334$_4$	0·332$_6$	0·330$_8$	0·329$_1$
35	0·327$_3$	0·325$_6$	0·323$_9$	0·322$_2$	0·320$_5$	0·318$_8$	0·317$_2$	0·315$_5$	0·313$_9$	0·312$_3$
36	0·310$_8$	0·308$_9$	0·307$_3$	0·305$_7$	0·304$_1$	0·302$_6$	0·300$_9$	0·299$_4$	0·297$_9$	0·296$_3$
37	0·294$_8$	0·293$_2$	0·291$_7$	0·290$_2$	0·288$_7$	0·287$_2$	0·285$_8$	0·284$_3$	0·282$_8$	0·281$_4$
38	0·280	0·278$_5$	0·277$_1$	0·275$_7$	0·274$_3$	0·272$_9$	0·271$_5$	0·270$_1$	0·268$_8$	0·267$_4$
39	0·266$_1$	0·264$_7$	0·263$_4$	0·262$_1$	0·260$_7$	0·259$_4$	0·258$_1$	0·236$_8$	0·255$_5$	0·254$_3$
40	0·253	0·251$_7$	0·250$_5$	0·249$_2$	0·248	0·246$_8$	0·245$_5$	0·244$_3$	0·243$_1$	0·241$_9$
41	0·240$_7$	0·239$_6$	0·238$_3$	0·237$_1$	0·236	0·234$_8$	0·233$_6$	0·232$_5$	0·231$_4$	0·230$_2$
42	0·229$_1$	0·228	0·226$_9$	0·225$_7$	0·224$_6$	0·223$_5$	0·222$_5$	0·221$_4$	0·220$_3$	0·219$_2$
43	0·218$_1$	0·217$_1$	0·216	0·215	0·213$_9$	0·212$_9$	0·211$_9$	0·210$_9$	0·209$_9$	0·208$_9$
44	0·207$_8$	0·206$_8$	0·205$_8$	0·204$_8$	0·203$_8$	0·202$_9$	0·201$_9$	0·200$_9$	0·200	0·199
45	0·198$_1$	0·197$_1$	0·198$_2$	0·195$_3$	0·194$_3$	0·193$_4$	0·192$_5$	0·191$_6$	0·190$_8$	0·189$_7$
46	0·188$_8$	0·187$_9$	0·187	0·186$_2$	0·185$_4$	0·184$_4$	0·183$_6$	0·182$_7$	0·181$_8$	0·180$_9$
47	0·180$_1$	0·179$_2$	0·178$_4$	0·177$_6$	0·176$_7$	0·175$_9$	0·175$_1$	0·174$_3$	0·173$_4$	0·172$_6$
48	0·171$_8$	0·171	0·170$_2$	0·169$_4$	0·168$_6$	0·167$_9$	0·167$_1$	0·166$_3$	0·165$_6$	0·164$_9$
49	0·164	0·163$_3$	0·162$_5$	0·161$_7$	0·161	0·160$_3$	0·159$_6$	0·158$_7$	0·158	0·157$_3$
50	0·156$_6$	0·155$_8$	0·155$_1$	0·154$_4$	0·153$_7$	0·153	0·152$_3$	0·151$_6$	0·150$_9$	0·150$_2$
51	0·149$_5$	0·148$_8$	0·148$_1$	0·147$_4$	0·146$_8$	0·146$_1$	0·145$_4$	0·144$_8$	0·144$_1$	0·143$_4$
52	0·142$_8$	0·142$_1$	0·141$_5$	0·140$_8$	0·140$_2$	0·139$_6$	0·138$_9$	0·138$_3$	0·137$_7$	0·137$_1$
53	0·136$_4$	0·135$_8$	0·135$_2$	0·134$_6$	0·134	0·133$_4$	0·132$_8$	0·132$_2$	0·131$_6$	0·131
54	0·130$_4$	0·129$_8$	0·129$_2$	0·128$_6$	0·128	0·127$_5$	0·126$_9$	0·126$_3$	0·125$_8$	0·125$_2$
55	0·124$_6$	0·124$_1$	0·123$_5$	0·123	0·122$_4$	0·121$_9$	0·121$_3$	0·120$_8$	0·120$_3$	0·119$_7$
56	0·1192	0·1186	0·1181	0·1176	0·1171	0·1165	0·116	0·1155	0·115	0·1145
57	0·1140	0·1135	0·1130	0·1125	0·1120	0·1115	0·1110	0·1105	0·1100	0·1095
58	0·1090	0·1085	0·1080	0·1076	0·1071	0·1066	0·1062	0·1057	0·1052	0·1048
59	0·1043	0·1038	0·1034	0·1029	0·1025	0·1020	0·1016	0·1011	0·1007	0·1002
60	0·0998	0·0994	0·0989	0·0985	0·0981	0·0976	0·0972	0·0968	0·0963	0·0959
61	0·0955	0·0951	0·0946$_5$	0·0942$_5$	0·0938$_5$	0·0934	0·0930	0·0926	0·0922	0·0918
62	0·0914	0·0910	0·0906	0·0902	0·0898	0·0894$_5$	0·0890$_5$	0·0886$_5$	0·0882$_5$	0·0879
63	0·0875	0·0871	0·0867$_5$	0·0863$_5$	0·0860	0·0856	0·0852$_5$	0·0849	0·0845	0·0841$_5$
64	0·0838	0·0834	0·0830$_5$	0·0827	0·0823$_5$	0·0820	0·0816$_5$	0·0813	0·0809$_5$	0·0806
65	0·0802$_5$	0·0799	0·0795$_5$	0·0792	0·0788$_5$	0·0785	0·0782	0·0778$_5$	0·0775	0·0772
66	0·0768$_5$	0·0765	0·0762	0·0758$_5$	0·0755$_5$	0·0752	0·0749	0·0745$_5$	0·0742$_5$	0·0739$_5$
67	0·0736	0·0733	0·0730	0·0726$_5$	0·0723$_5$	0·0720$_5$	0·0717$_5$	0·0714$_5$	0·0711$_5$	0·0708
68	0·0705	0·0702	0·0699	0·0696	0·0693	0·0690$_5$	0·0687$_5$	0·0684$_5$	0·0681$_5$	0·0678$_5$
69	0·0675$_5$	0·0673	0·0670	0·0667	0·0664	0·0661$_5$	0·0658$_5$	0·0656	0·0653	0·0650

TABLE I (*contd.*).

ε.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
70	0·0647$_5$	0·0644$_5$	0·0642	0·0639$_5$	0·0636$_5$	0·0634	0·0631	0·0628$_5$	0·0626	0·0623
71	0·0620$_5$	0·0618	0·0615$_5$	0·0612$_5$	0·0610	0·0607$_5$	0·0605	0·0602$_5$	0·0600	0·0597$_5$
72	0·0594$_5$	0·0592	0·0589$_5$	0·0587	0·0584$_5$	0·0582$_5$	0·0580	0·0577$_5$	0·0575	0·0572$_5$
73	0·0570	0·0567$_5$	0·0565$_5$	0·0563	0·0560$_5$	0·0558	0·0556	0·0553$_5$	0·0551	0·0549
74	0·0546$_5$	0·0544	0·0542	0·0539$_5$	0·0537$_5$	0·0535	0·0533	0·0530$_5$	0·0528$_5$	0·0526
75	0·0524	0·0522	0·0519$_5$	0·0517$_5$	0·0515	0·0513	0·0511	0·0509	0·0506$_5$	0·0504$_5$
76	0·0502$_5$	0·0500$_5$	0·0498	0·0496	0·0494	0·0492	0·0490	0·0488	0·0486	0·0484
77	0·0481$_5$	0·0479$_5$	0·0477$_5$	0·0475$_5$	0·0473$_5$	0·0471$_5$	0·0470	0·0468	0·0466	0·0464
78	0·0462	0·0460	0·0458	0·0456	0·0454$_5$	0·0452$_5$	0·0450$_5$	0·0448$_5$	0·0447	0·0445
79	0·0443	0·0441	0·0439$_5$	0·0437$_5$	0·0435$_5$	0·0434	0·0432	0·0430$_5$	0·0428$_5$	0·0426
80	0·0425	0·0423	0·0421$_5$	0·0419$_5$	0·0418	0·0416	0·0414$_5$	0·0412$_5$	0·0411	0·0409
81	0·0407$_5$	0·0406	0·0404	0·0402$_5$	0·0401	0·0399	0·0397$_5$	0·0396	0·0394$_5$	0·0392
82	0·0391	0·0389$_5$	0·0388	0·0386	0·0384$_5$	0·0383	0·0381$_5$	0·0380	0·0378	0·0376
83	0·0375	0·0373$_5$	0·0372	0·0370$_5$	0·0369	0·0367$_5$	0·0366	0·0364$_5$	0·0363	0·0361
84	0·0360	0·0358$_5$	0·0357	0·0355$_5$	0·0354	0·0352$_5$	0·0351	0·0349$_5$	0·0348	0·0346
85	0·0345$_5$	0·0344	0·0342$_5$	0·0341	0·0339$_5$	0·0338	0·0337	0·0335$_5$	0·0334	0·0332
86	0·0331$_5$	0·0330	0·0328$_5$	0·0327	0·0326	0·0324$_5$	0·0323	0·0322	0·0320$_5$	0·0319
87	0·0318	0·0316$_5$	0·0315$_5$	0·0314	0·0312$_5$	0·0311$_5$	0·0310	0·0309	0·0307$_5$	0·0306
88	0·0305	0·0304	0·0302$_5$	0·0301$_5$	0·0300	0·0299	0·0297$_5$	0·0296$_5$	0·0295	0·0294
89	0·0292$_5$	0·0291$_5$	0·0290$_5$	0·0289	0·0288	0·0287	0·0285$_5$	0·0284$_5$	0·0283	0·0282
90	0·0281	0·0280	0·0278$_5$	0·0277$_5$	0·0276$_5$	0·0275	0·0274	0·0273	0·0272	0·0270
91	0·0269$_5$	0·0268$_5$	0·0267$_5$	0·0266$_5$	0·0265	0·0264	0·0263	0·0262	0·0261	0·0260
92	0·0259	0·0257$_5$	0·0256$_5$	0·0255$_5$	0·0254$_5$	0·0253$_5$	0·0252$_5$	0·0251$_5$	0·0250$_5$	0·0249$_5$
93	0·0248$_5$	0·0247$_5$	0·0246$_5$	0·0245$_5$	0·0244$_5$	0·0243$_5$	0·0242$_5$	0·0241$_5$	0·0240$_5$	0·0239$_5$
94	0·0238$_5$	0·0237$_5$	0·0236$_5$	0·0235$_5$	0·0234$_5$	0·0233$_5$	0·0232$_5$	0·0231$_5$	0·0230$_5$	0·0230
95	0·0229	0·0228	0·0227	0·0226	0·0225	0·0224	0·0223$_5$	0·0222$_5$	0·0221$_5$	0·0220$_5$
96	0·0219$_5$	0·0219	0·0218	0·0217	0·0216	0·0215	0·0214$_5$	0·0213$_5$	0·0212$_5$	0·0211$_5$
97	0·0211	0·0210	0·0209	0·0208$_5$	0·0207$_5$	0·0206$_5$	0·0206	0·0205	0·0204	0·0203$_5$
98	0·0202$_5$	0·0201$_5$	0·0201	0·0200	0·0199	0·0198$_5$	0·0197$_5$	0·0196$_5$	0·0196	0·0195
99	0·0194$_5$	0·0193$_5$	0·0193	0·0192	0·0191	0·0190$_5$	0·0189$_5$	0·0189	0·0188	0·0187$_5$
ε.	+0.	+1.	+2.	+3.	+4.	+5.	+6.	+7.	+8.	+9.
100	0·0186$_5$	0·0179	0·0172	0·0165	0·0158$_5$	0·0152	0·0146	0·0140$_5$	0·0135	0·0129
110	0·0124$_5$	0·0119$_5$	0·0114$_5$	0·0110	0·0105$_5$	0·0101$_5$	0·0097$_5$	0·0093$_5$	0·0090	0·0086$_5$
120	0·0083	0·0079$_5$	0·0076$_5$	0·0073$_5$	0·0070$_5$	0·0068	0·0065	0·0062$_5$	0·0060	0·0057$_5$
130	0·0055$_5$	0·0053$_5$	0·0051	0·0049	0·0047	0·0045$_5$	0·0043$_5$	0·0042	0·0040	0·0038
140	0·0037	0·0035$_5$	0·0034$_5$	0·0033	0·0031$_5$	0·0030$_5$	0·0029	0·0028	0·0027	0·0026
150	0·0025	0·0024	0·0023	0·0022	0·0021	0·0020$_5$	0·0019$_5$	0·0019	0·0018	0·0017$_5$
160	0·0016$_5$	0·0016	0·0015$_5$	0·0015	0·0014	0·0013$_5$	0·0013	0·0012$_5$	0·0012	0·0011$_5$
170	0·0011	0·0010$_5$	0·0010$_5$	0·0010	0·0009$_5$	0·0009	0·0009	0·0008$_5$	0·0008	0·0008
180	0·0007$_5$	0·0007	0·0007	0·0006$_5$	0·0006$_5$	0·0006	0·0006	0·0005$_5$	0·0005$_5$	0·0005
190	0·0005	0·0005	0·0004$_5$	0·0004$_5$	0·0004$_5$	0·0004	0·0004	0·0004	0·0003$_5$	0·0003$_5$

TABLE II.

$$\varepsilon_v = f^{-1}(1/x) = RT/F \, . \log (1 + x).$$

$x = m/V'$ or m/V_0; $T = 290°$ Abs.

x.	·00.	·01.	·02.	·03.	·04.	·05.	·06.	·07.	·08.	·09.
0·0	0·00	0·2$_5$	0·5	0·7$_4$	0·9$_8$	1·2$_2$	1·4$_6$	1·6$_9$	1·9$_2$	2·1$_5$
0·1	2·3$_8$	2·6$_1$	2·8$_3$	3·0$_6$	3·2$_8$	3·4$_9$	3·7$_1$	3·9$_3$	4·1$_4$	4·3$_5$
0·2	4·5$_6$	4·7$_7$	4·9$_7$	5·1$_8$	5·3$_8$	5·5$_8$	5·7$_8$	5·9$_8$	6·1$_7$	6·3$_7$
0·3	6·5$_6$	6·7$_5$	6·9$_4$	7·1$_3$	7·3$_2$	7·5	7·6$_9$	7·8$_7$	8·0$_5$	8·2$_3$
0·4	8·4$_1$	8·5$_9$	8·7$_7$	8·9$_4$	9·1$_2$	9·2$_9$	9·4$_6$	9·6$_3$	9·8	9·9$_7$
0·5	10·1$_4$	10·3	10·4$_7$	10·6$_3$	10·7$_9$	10·9$_6$	11·1$_2$	11·2$_8$	11·4$_4$	11·5$_9$
0·6	11·7$_5$	11·9$_1$	12·0$_6$	12·2$_1$	12·3$_7$	12·5$_2$	12·6$_7$	12·8$_2$	12·9$_7$	13·1$_2$
0·7	13·2$_7$	13·4$_1$	13·5$_6$	13·7	13·8$_5$	13·9$_9$	14·1$_3$	14·2$_7$	14·4$_2$	14·5$_6$
0·8	14·6$_9$	14·8$_3$	14·9$_7$	15·1$_1$	15·2$_4$	15·3$_8$	15·5$_1$	15·6$_5$	15·7$_8$	15·9$_1$
0·9	16·0$_5$	16·1$_8$	16·3$_1$	16·4$_4$	16·5$_7$	16·7	16·8$_2$	16·9$_5$	17·0$_8$	17·2
1·0	17·3$_3$	17·4$_5$	17·5$_8$	17·7	17·8$_2$	17·9$_5$	18·0$_7$	18·1$_9$	18·3$_1$	18·4$_3$
1·1	18·5$_5$	18·6$_7$	18·7$_9$	18·9	19·0$_2$	19·1$_4$	19·2$_5$	19·3$_7$	19·4$_8$	19·6
1·2	19·7$_1$	19·8$_3$	19·9$_4$	20·0$_5$	20·1$_6$	20·2$_7$	20·3$_8$	20·4$_9$	20·6	20·7$_1$
1·3	20·8$_2$	20·9$_3$	21·0$_4$	21·1$_5$	21·2$_5$	21·3$_6$	21·4$_7$	21·5$_7$	21·6$_8$	21·7$_8$
1·4	21·8$_9$	21·9$_9$	22·0$_9$	22·2	22·3	22·4	22·5	22·6$_1$	22·7$_1$	22·8$_1$
1·5	22·9$_1$	23·0$_1$	23·1$_1$	23·2$_1$	23·3	23·4	23·5	23·6	23·6$_9$	23·7$_9$
1·6	23·8$_9$	23·9$_8$	24·0$_8$	24·1$_7$	24·2$_7$	24·3$_6$	24·4$_6$	24·5$_5$	24·6$_5$	24·7$_4$
1·7	24·8$_3$	24·9$_2$	25·0$_2$	25·1$_1$	25·2	25·2$_9$	25·3$_8$	25·4$_7$	25·5$_6$	25·6$_5$
1·8	25·7$_4$	25·8$_3$	25·9$_2$	26·0$_1$	26·1	26·1$_8$	26·2$_7$	26·3$_6$	26·4$_4$	26·5$_3$
1·9	26·6$_2$	26·7	26·7$_9$	26·8$_8$	26·9$_6$	27·0$_5$	27·1$_3$	27·2$_1$	27·3	27·3$_8$
2·0	27·4	[illegible]	27·6	27·7	27·8	27·8	27·9	28·0	28·1	28·2

This table gives ε_v (in millivolts), the change in the potential E due to the dilution of the solution from V' c.c. to $(V' + m)$ c.c., the change being in the same direction as the change due to adding the reagent.

TABLE IIA.

$$\varepsilon_v = f^{-1}(1/x - 1) = -RT/F.\log(1 - x).$$

$$x = m/V\,;\; T = 290^\circ \text{ Abs.}$$

x.	·00.	·01.	·02.	·03.	·04.	·05.	·06.	·07.	·08.	·09.
0·0	0·00	$0{\cdot}2_5$	0·5	$0{\cdot}7_6$	$1{\cdot}0_2$	$1{\cdot}2_8$	$1{\cdot}5_5$	$1{\cdot}8_1$	$2{\cdot}0_8$	$2{\cdot}3_6$
0·1	$2{\cdot}6_3$	$2{\cdot}9_1$	3·2	$3{\cdot}4_8$	$3{\cdot}7_7$	$4{\cdot}0_6$	$4{\cdot}3_6$	$4{\cdot}6_6$	$4{\cdot}9_6$	$5{\cdot}2_7$
0·2	$5{\cdot}5_8$	$5{\cdot}8_9$	$6{\cdot}2_1$	$6{\cdot}5_3$	$6{\cdot}8_6$	$7{\cdot}1_9$	$7{\cdot}5_3$	$7{\cdot}8_7$	$8{\cdot}2_1$	$8{\cdot}5_6$
0·3	$8{\cdot}9_2$	$9{\cdot}2_8$	$9{\cdot}6_4$	$10{\cdot}0_1$	$10{\cdot}3_9$	$10{\cdot}7_7$	$11{\cdot}1_6$	$11{\cdot}5_5$	$11{\cdot}9_5$	$12{\cdot}3_6$
0·4	$12{\cdot}7_7$	$13{\cdot}1_9$	$13{\cdot}6_2$	$14{\cdot}0_5$	14·5	$14{\cdot}9_5$	15·4	$15{\cdot}8_7$	$16{\cdot}3_5$	$16{\cdot}8_3$
0·5	$17{\cdot}3_3$	$17{\cdot}8_3$	$18{\cdot}3_5$	$18{\cdot}8_8$	$19{\cdot}4_1$	$19{\cdot}9_6$	$20{\cdot}5_2$	21·1	$21{\cdot}6_9$	$22{\cdot}2_9$

This table gives ε_v (in millivolts), the change in the potential E due to dilution of the solution from $(V - m)$ c.c. to V c.c., the change being in the same direction as the change due to adding the reagent.

13. There is an alternative way of allowing for the change in the volume of the solution, which is of interest in that it completes the connexion between the simple method now described and the more refined methods of Part II. Equation (19) may be written,

$$\varepsilon = RT/F.\log V(M + m)/M(V - m)$$
$$= RT/F.\log\,[1 + m(V + M)/M(V - m)]$$

i.e., $$f(\varepsilon) = r \qquad (28)$$

where $$r = M(V - m)/m(V + M) \qquad (29)$$

whence $$M = rm/[1 - m(1 + r)/V] \qquad (30)$$

[compare Part II, equation (19)], which reduces to equation (7) when m/V is negligible (constant volume). This way of allowing for the changing volume of the solution seems, however, to be less simple and expeditious than the application of the correction ε_v to the measured potential change (Sections 2 and 11), or the correction of the measured potentials according to Sections 11 and 12.

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CXVI.—*Differential Potentiometric Titration. Part II. Refined Methods (Methods II and III).*

By BERNARD CAVANAGH.

1. *An Equation to the Titration Curve.*—In considering the procedure by which the highest degree of precision is to be obtained, it will be convenient to confine attention in the first place to the typical case of the titration of a chloride by means of silver nitrate.

The extension to other titrations depending on the combination or interaction of ions of like valency will then be obvious.

If s^2 is the activity product of silver chloride (so that s is practically the solubility in pure water), c' and c are the concentrations and γ' and γ the activity coefficients of silver and chloride ions, respectively,

$$c \, . \, \gamma \, . \, c' \, . \, \gamma' = s^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

So long as the reagent can be considered to react completely with the titrated solution, no appreciable amount of silver ion remaining free, the quantity M c.c. of reagent still required must be chemically equivalent to the whole of the free chloride ion, *i.e.*, there must be Mn mg.-equivs. of free chloride ion present, n being the normality of the reagent solution. In view of the presence of a precipitate, however, it cannot be assumed that the whole of this is *in solution*, for a certain fraction of it $(1 - \theta)$, will, in general, be adsorbed by the precipitate [although in the titration of very dilute solutions, to which the refined method chiefly applies, the amount of precipitate is slight and the fraction $(1 - \theta)$ probably very small—compare preceding paper, Section 7]. The concentration c will therefore be $Mn\theta/V$, V being the volume o solution, *i.e.*,

$$Mn = cV/\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

When the end-point is closely approached, however, the free silve ion can no longer be neglected. Suppose the fraction $(1 - \theta')$ o the total free silver ion is in the adsorbed condition, then the amoun of reagent required will be reduced by the corresponding amoun $c'V/\theta'$, so that

$$Mn = cV/\theta - c'V/\theta' \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The potential of a (reversible) silver electrode dipping in th solution is (at constant temperature)

$$E = \text{constant} - RT/F \, . \log c'\gamma' \quad . \quad . \quad . \quad (4)$$

whilst that of a chloride electrode is

$$E = \text{constant} + RT/F \, . \log c\gamma \quad . \quad . \quad . \quad . \quad (5)$$

and from equations (1), (3), and *either* (4) or (5), one obtai rigorously,

$$\frac{Mn\sqrt{\gamma\gamma'\theta\theta'}}{2s(V_e - M)} = \sinh\left[\frac{F}{RT}(E - E_e) + \tfrac{1}{2}\log\frac{\gamma'\gamma_e}{\gamma\gamma_e'} + \tfrac{1}{2}\log\frac{\theta'\theta_e}{\theta\theta_e'} \pm \log\frac{s}{s_e}\right] (6)$$

where the suffix e denotes the end-point value of a quantity, ar of the alternative signs, the positive is obtained by using equation and the negative by using equation (5). In this equation, ap from s and the coefficients γ, γ', θ, θ', whose variations can be k

small, the only variables at constant temperature are M and E, and both variables may have any values, positive or negative.

This exact and complete equation to the titration curve is of the form

$$X = \sinh U \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which lends itself to mathematical treatment, with results which are immediately useful, since hyperbolic functions are fully tabulated. It is applicable (when suitable electrodes are available) to (*a*) other precipitations of insoluble uni-univalent salts if the appropriate activity product s is used; (*b*) precipitations of ν-ν-valent insoluble salts if νF and n/ν are substituted for F and n, respectively; (*c*) the titration of strong acid and alkali (in the complete absence of carbon dioxide, ammonia, quinhydrone, etc.)—the adsorption factors disappear, and s represents the activity product of water; and (*d*) the last titration in the presence of carbon dioxide, etc., with certain limitations.

2. For present purposes equation (6) may be written in the simplified form

$$Mn/2S(V_e - M) = \sinh F(E - E_e)/RT \quad . \quad . \quad (8)$$

where $$S^2 = s^2/\gamma\gamma'\theta\theta' \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

S^2 being, as it were, an "apparent" solubility product of silver chloride (including both dissolved and adsorbed) in the solution at *the stage under consideration.* This approximation involves neglecting (*a*) the term $\pm \log s/s_e$, which allows for variation in s during the course of a titration (due, for instance, to change in the condition of the precipitate), and (*b*) the other two logarithmic terms.

In the case chiefly considered here, that of the silver chloride titration, it would seem reasonable to expect that the presence of the silver chloride-coated electrodes (see J., 1927, 2207) would tend to accelerate the establishment of true equilibrium (with the minimum value of s) and make s effectively a constant, and this appears to be borne out by the steadiness and permanence of the potentials rapidly set up. In the case of the bromide titration, conditions are almost equally good (with the silver bromide-coated electrodes), but in the iodide titration, in the neighbourhood of the end-point the establishment of a permanent potential is very slow.

As regards the other two neglected terms it may be noted that γ'/γ, for instance, is the ratio of the activity coefficients of univalent ions in the same solution, and that the first logarithmic term, representing half the relative change in this ratio on passing over to the end-point, will always be very small. Similar considerations apply to the second logarithmic term.

TABLE I.

Figures in heavy type, sinh $(F/RT) \,.\, E$. Figures in ordinary type, sech $(F/RT) \,.\, E$ (at 17°).

E in m.v.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
0	**0·000** 1·000	**0·004** 1·000	**0·008** 1·000	**0·012** 0·999$_9$	**0·016** 0·999$_8$	**0·020** 0·999$_8$	**0·024** 0·999$_7$	**0·028** 0·999$_6$	**0·032** 0·999$_5$	**0·036** 0·999$_4$
1	**0·040** 0·999$_3$	**0·044** 0·999	**0·048** 0·998$_8$	**0·052** 0·998$_6$	**0·056** 0·998$_4$	**0·060** 0·998$_2$	**0·064** 0·998	**0·068** 0·997$_7$	**0·072** 0·997$_4$	**0·078** 0·997$_1$
2	**0·080** 0·996$_9$	**0·084** 0·996$_5$	**0·088** 0·996$_1$	**0·092** 0·995$_8$	**0·096** 0·995$_4$	**0 100** 0·995	**0·104** 0·994$_6$	**0·108** 0·994$_2$	**0·112** 0·993$_8$	**0·116** 0·993$_3$
3	**0·120** 0·992$_8$	**0 124** 0·992$_4$	**0·128** 0·991$_9$	**0·132** 0·991$_3$	**0·136** 0·990$_8$	**0·140** 0·990$_3$	**0·145** 0·989$_7$	**0·149** 0·989$_1$	**0·153** 0·988$_6$	**0·157** 0·988
4	**0·161** 0·987$_3$	**0 165** 0·986$_7$	**0·169** 0·986$_1$	**0·173** 0·985$_4$	**0 177** 0·984$_7$	**0·181** 0·984	**0·185** 0·983$_3$	**0·189** 0·982$_6$	**0·193** 0·981$_9$	**0·197** 0·981$_1$
5	**0·202** 0·980$_3$	**0·205** 0·979$_5$	**0·210** 0·978$_6$	**0·214** 0·977$_9$	**0·218** 0·977$_1$	**0·222** 0·976$_3$	**0·226** 0·975$_4$	**0·230** 0·974$_6$	**0·234** 0·973$_7$	**0·238** 0·972$_8$
6	**0·242** 0·971$_9$	**0·246** 0·971	**0·251** 0·970	**0·255** 0·969$_1$	**0·259** 0·978$_1$	**0·203** 0·967$_1$	**0·267** 0·966$_1$	**0·271** 0·965$_1$	**0·275** 0·964$_1$	**0·280** 0·963$_1$
7	**0·284** 0·962	**0·288** 0·961	**0·292** 0·959$_9$	**0·296** 0·958$_8$	**0·300** 0·957$_7$	**0·305** 0·956$_6$	**0·309** 0·955$_5$	**0·313** 0·954$_4$	**0·317** 0·953$_3$	**0·331** 0·952$_1$
8	**0·325** 0·950$_9$	**0·330** 0·949$_7$	**0·334** 0·948$_5$	**0·338** 0·947$_3$	**0·342** 0·946$_1$	**0·347** 0·944$_9$	**0·351** 0·943$_6$	**0·355** 0·942$_4$	**0·359** 0·941$_1$	**0·304** 0·939$_8$
9	**0·368** 0·938$_5$	**0·372** 0·937$_2$	**0·376** 0·935$_9$	**0·381** 0·934$_6$	**0·385** 0·933$_2$	**0·389** 0·931$_9$	**0·394** 0·930$_5$	**0·398** 0·929$_1$	**0·402** 0·927$_8$	**0·406** 0·926$_4$
10	**0·411** 0·925	**0·415** 0·923$_6$	**0·419** 0·922$_2$	**0·424** 0·920$_7$	**0·428** 0·919$_3$	**0·432** 0·917$_8$	**0·437** 0·916$_4$	**0·441** 0·914$_9$	**0·446** 0·913$_4$	**0·450** 0·911$_9$
11	**0·454** 0·910$_4$	**0·459** 0·908$_9$	**0·463** 0·907$_4$	**0·468** 0·905$_9$	**0·472** 0·904$_3$	**0·476** 0·902$_8$	**0·481** 0·901$_3$	**0·485** 0·899$_7$	**0·490** 0·898$_1$	**0·494** 0·896$_5$
12	**0·499** 0·894$_9$	**0·503** 0·893$_3$	**0·508** 0·891$_7$	**0·512** 0·890$_1$	**0·517** 0·888$_5$	**0·521** 0·886$_8$	**0·526** 0·885$_2$	**0·530** 0·883$_5$	**0·535** 0·881$_9$	**0·539** 0·880$_2$
13	**0·544** 0·878$_5$	**0·548** 0·876$_8$	**0·553** 0·875$_1$	**0·557** 0·873$_4$	**0·562** 0·871$_7$	**0·566** 0·870	**0·571** 0·868$_3$	**0·576** 0·866$_6$	**0·580** 0·864$_9$	**0·585** 0·863$_1$
14	**0·590** 0·861$_4$	**0·594** 0·859$_6$	**0·599** 0·857$_9$	**0·604** 0·856$_1$	**0·608** 0·854$_3$	**0·613** 0·852$_5$	**0·618** 0·850$_8$	**0·622** 0·849	**0·627** 0·847$_2$	**0·632** 0·845$_4$
15	**0·637** 0·843$_6$	**0·641** 0·841$_7$	**0·646** 0·839$_9$	**0·651** 0·838$_1$	**0·656** 0·836$_3$	**0·660** 0·834$_4$	**0·665** 0·832$_6$	**0·670** 0·830$_7$	**0·675** 0·828$_9$	**0·680** 0·827
16	**0·685** 0·825$_2$	**0·690** 0·823$_3$	**0·694** 0·821$_4$	**0·699** 0·819$_5$	**0·704** 0·817$_7$	**0·709** 0·815$_8$	**0·714** 0·813$_9$	**0·719** 0·812	**0·724** 0·810$_1$	**0·729** 0·808$_2$
17	**0·734** 0·806$_3$	**0·739** 0·804$_4$	**0·744** 0·802$_5$	**0·749** 0·800$_6$	**0·754** 0·798$_6$	**0·759** 0·796$_7$	**0·764** 0·794$_8$	**0·769** 0·792$_8$	**0·774** 0·790$_9$	**0·779** 0·789
18	**0·784** 0·787	**0 789** 0·785$_1$	**0 794** 0·783$_1$	**0·799** 0·781$_2$	**0·804** 0·779$_2$	**0·809** 0·777$_3$	**0·815** 0·775$_3$	**0·820** 0·773$_4$	**0·825** 0·771$_4$	**0·830** 0·769$_4$
19	**0·835** 0·767$_5$	**0·840** 0·765$_5$	**0·846** 0·763$_5$	**0·851** 0·761$_6$	**0·856** 0·769$_6$	**0·862** 0·757$_6$	**0·867** 0·755$_6$	**0·872** 0·753$_7$	**0·877** 0·751$_7$	**0·883** 0·749$_7$
20	**0·888** 0·747$_7$	**0·894** 0·745$_7$	**0·899** 0·743$_7$	**0·904** 0·741$_7$	**0·910** 0·739$_7$	**0·915** 0·737$_8$	**0·920** 0·735$_8$	**0·926** 0·733$_8$	**0·931** 0·731$_8$	**0·937** 0·729$_8$
21	**0·942** 0·727$_8$	**0·948** 0·725$_8$	**0·953** 0·723$_8$	**0·959** 0·721$_8$	**0·964** 0·719$_8$	**0·970** 0·717$_8$	**0·976** 0·715$_8$	**0·981** 0·713$_8$	**0·987** 0·711$_8$	**0·992** 0·709$_8$
22	**0,998** 0·707$_8$	**1·004** 0·705$_8$	**1·009** 0·703$_8$	**1·015** 0·701$_8$	**1·021** 0·699$_8$	**1·027** 0·697$_8$	**1·032** 0·695$_8$	**1·038** 0·693$_8$	**1·044** 0·691$_8$	**1·050** 0·689$_8$
23	**1·055** 0·687$_8$	**1·061** 0·685$_8$	**1·067** 0·683$_8$	**1·073** 0·681$_8$	**1·079** 0·679$_8$	**1·085** 0·677$_8$	**1·091** 0·675$_8$	**1·097** 0·673$_8$	**1·102** 0·671$_9$	**1·108** 0·669$_9$
24	**1·114** 0·667$_9$	**1·120** 0·665$_9$	**1·126** 0·663$_9$	**1·132** 0·661$_9$	**1·139** 0·659$_9$	**1·145** 0·657$_9$	**1·151** 0·656	**1·157** 0·654	**1·163** 0·652	**1·169** 0·650
25	**1·175** 0·648$_1$	**1·181** 0·646$_1$	**1·188** 0·644$_1$	**1·194** 0·642$_1$	**1·200** 0·640$_2$	**1·206** 0·638$_2$	**1·213** 0·636$_3$	**1·219** 0·634$_3$	**1·225** 0·632$_3$	**1·232** 0·630$_4$
26	**1·238** 0·628$_4$	**1·244** 0·626$_4$	**1 251** 0·624$_5$	**1·257** 0·622$_6$	**1·264** 0·620$_6$	**1·270** 0·618$_7$	**1·276** 0·616$_7$	**1·283** 0·614$_8$	**1·289** 0·612$_8$	**1·296** 0·610$_9$
27	**1·303** 0·609	**1·309** 0·607	**1·315** 0·605$_1$	**1·322** 0·603$_2$	**1·329** 0·601$_3$	**1·336** 0·599$_3$	**1·342** 0·597$_4$	**1·349** 0·595$_5$	**1·356** 0·593$_6$	**1·363** 0·591$_7$
28	**1·369** 0·589$_8$	**1·376** 0·587$_9$	**1·383** 0·586	**1·390** 0·584$_1$	**1·397** 0·582$_2$	**1·403** 0·580$_3$	**1·410** 0·578$_4$	**1·417** 0·576$_5$	**1·424** 0·574$_6$	**1·431** 0·572$_7$
29	**1·438** 0·570$_9$	**1·445** 0·569	**1·452** 0·567$_1$	**1·459** 0·565$_2$	**1·466** 0·563$_4$	**1·474** 0·561$_5$	**1·481** 0·559$_7$	**1·488** 0·557$_8$	**1·495** 0·556	**1·502** 0·554$_1$
30	**1·509** 0·552$_3$	**1·517** 0·550$_4$	**1·524** 0·548$_6$	**1·531** 0·546$_8$	**1·539** 0·544$_9$	**1·546** 0·543$_1$	**1·553** 0·541$_3$	**1·561** 0·539$_5$	**1·568** 0·537$_7$	**1·576** 0·535
31	**1·583** 0·534	**1·591** 0·532$_2$	**1·598** 0·530$_4$	**1·606** 0·528$_6$	**1·613** 0·526$_9$	**1·621** 0·525$_1$	**1·629** 0·523$_3$	**1·636** 0·521$_5$	**1·644** 0·519$_7$	**1·652** 0·517
32	**1·659** 0·516$_2$	**1·667** 0·514$_4$	**1·675** 0·512$_6$	**1·683** 0·510$_9$	**1·691** 0·509$_1$	**1·698** 0·507$_4$	**1·706** 0·505$_6$	**1·714** 0·503$_9$	**1·722** 0·502$_1$	**1·730** 0·500
33	**1·738** 0·498$_7$	**1·746** 0·497	**1·754** 0·495$_2$	**1·762** 0·493$_5$	**1·770** 0·491$_8$	**1·779** 0·490$_1$	**1·787** 0·488$_4$	**1·795** 0·486$_7$	**1·803** 0·485	**1·811** 0·483
34	**1·820** 0·481$_5$	**1·828** 0·479$_9$	**1·836** 0·478$_2$	**1·845** 0·476$_6$	**1·853** 0·474$_9$	**1·862** 0·473$_3$	**1·870** 0·471$_6$	**1·879** 0·469$_9$	**1·887** 0·468$_3$	**1·896** 0·466

TABLE I (*contd.*).

E in m.v.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
	1·904	**1·913**	**1·922**	**1·930**	**1·939**	**1·948**	**1·956**	**1·965**	**1·974**	**1·983**
35	0·464$_4$	0·463$_3$	0·461$_6$	0·460	0·458$_4$	0·456$_7$	0·455$_1$	0·453$_5$	0·451$_9$	0·450$_3$
	1·992	**2·001**	**2·010**	**2·023**	**2·028**	**2·037**	**2·046**	**2·055**	**2·064**	**2·073**
36	0·448$_7$	0·447$_1$	0·445$_5$	0·443$_9$	0·442$_3$	0·440$_7$	0·439$_1$	0·437$_5$	0·436	0·434$_4$
	2·083	**2·092**	**2·101**	**2·111**	**2·130**	**2·129**	**2·139**	**2·148**	**2·158**	**2·107**
37	0·432$_8$	0·431$_3$	0·429$_7$	0·428$_2$	0·426$_6$	0·425$_1$	0·423$_6$	0·422	0·420$_5$	0·419
	2·177	**2·186**	**2·196**	**2·206**	**2·215**	**2·225**	**2·235**	**2·245**	**2·255**	**2·264**
38	0·417$_5$	0·415$_9$	0·414$_4$	0·412$_9$	0·411$_4$	0·409$_9$	0·408$_4$	0·406$_9$	0·405$_5$	0·404
	2·274	**2·284**	**2·294**	**2·304**	**2·314**	**2·324**	**2·335**	**2·345**	**2·355**	**2·365**
39	0·402$_5$	0·401	0·339$_6$	0·398$_1$	0·396$_6$	0·395$_2$	0·393$_7$	0·392$_3$	0·390$_8$	0·389$_4$
	2·376	**2·386**	**2·396**	**2·407**	**2·417**	**2·428**	**2·438**	**2·449**	**2·459**	**2·470**
40	0·388	0·386$_5$	0·385$_1$	0·383$_7$	0·382$_3$	0·380$_9$	0·379$_5$	0·378$_1$	0·376$_7$	0·375$_3$
	2·481	**2·491**	**2·502**	**2·513**	**2·524**	**2·535**	**2·546**	**2·556**	**2·567**	**2·579**
41	0·373$_9$	0·372$_5$	0·371$_1$	0·369$_7$	0·368$_4$	0·367	0·365$_6$	0·364$_3$	0·362$_9$	0·361$_6$
	2·590	**2·601**	**2·612**	**2·623**	**2·634**	**2·646**	**2·657**	**2·668**	**2·680**	**2·691**
42	0·360$_2$	0·358$_9$	0·357$_6$	0·356$_2$	0·354$_9$	0·353$_6$	0·352$_2$	0·350$_9$	0·349$_6$	0·348$_3$
	2·703	**2·714**	**2·726**	**2·738**	**2·749**	**2·761**	**2·773**	**2·784**	**2·796**	**2·808**
43	0·347	0·345$_7$	0·344$_4$	0·343$_1$	0·341$_8$	0·340$_5$	0·339$_3$	0·338	0·336$_7$	0·335$_5$
	2·820	**2·832**	**2·844**	**2·856**	**2·868**	**2·881**	**2·893**	**2·905**	**2·917**	**2·930**
44	0·334$_2$	0·332$_9$	0·331$_7$	0·330$_4$	0·329$_2$	0·327$_9$	0·326$_7$	0·325$_5$	0·324$_2$	0·323
	2·942	**2·955**	**2·967**	**2·980**	**2·992**	**3·005**	**3·018**	**3·030**	**3·043**	**3·056**
45	0·321$_8$	0·320$_6$	0·319$_4$	0·318$_2$	0·317	0·315$_8$	0·314$_6$	0·313$_4$	0·312$_2$	0·311
	3·069	**3·082**	**3·095**	**3·108**	**3·121**	**3·134**	**3·147**	**3·160**	**3·174**	**3·187**
46	0·309$_8$	0·308$_6$	0·307$_5$	0·306$_3$	0·305$_2$	0·304	0·302$_8$	0·301$_7$	0·300$_5$	0·299$_4$
	3·200	**3·214**	**3·227**	**3·241**	**3·255**	**3·268**	**3·282**	**3·296**	**3·309**	**3·323**
47	0·298$_2$	0·297$_1$	0·296	0·294$_8$	0·293$_7$	0·292$_6$	0·291$_5$	0·290$_4$	0·289$_3$	0·288$_2$
	3·337	**3·351**	**3·365**	**3·379**	**3·393**	**3·408**	**3·422**	**3·436**	**3·450**	**3·465**
48	0·287	0·285$_9$	0·284$_8$	0·283$_8$	0·282$_7$	0·281$_6$	0·280$_5$	0·279$_4$	0·278$_4$	0·277$_3$
	3·479	**3·494**	**3·508**	**3·523**	**3·538**	**3·552**	**3·577**	**3·582**	**3·597**	**3·622**
49	0·276$_2$	0·275$_2$	0·274$_1$	0·273$_1$	0·272	0·271	0·269$_9$	0·268$_9$	0·267$_9$	0·266$_8$
	3·627	**3·642**	**3·657**	**3·672**	**3·688**	**3·703**	**3·718**	**3·734**	**3·749**	**3·765**
50	0·265$_8$	0·264$_8$	0·263$_8$	0·262$_7$	0·261$_7$	0·260$_7$	0·259$_7$	0·258$_7$	0·257$_7$	0·256$_7$
	3·780	**3·796**	**3·812**	**3·827**	**3·843**	**3·859**	**3·875**	**3·891**	**3·907**	**3·924**
51	0·255$_7$	0·254$_7$	0·253$_8$	0·252$_8$	0·251$_8$	0·250$_8$	0·249$_9$	0·248$_9$	0·247$_9$	0·247
	3·940	**3·956**	**3·972**	**3·989**	**4·005**	**4·022**	**4·038**	**4·055**	**4·072**	**4·039**
52	0·246	0·245$_1$	0·244$_1$	0·243$_2$	0·242$_3$	0·241$_3$	0·240$_4$	0·239$_4$	0·238$_5$	0·237$_6$
	4·106	**4·122**	**4·139**	**4·157**	**4·174**	**4·191**	**4·208**	**4·225**	**4·243**	**4·260**
53	0·236$_7$	0·235$_7$	0·234$_8$	0·233$_9$	0·233	0·232$_1$	0·231$_2$	0·230$_3$	0·229$_4$	0·228$_5$
	4·278	**4·216**	**4·313**	**4·331**	**4·349**	**4·367**	**4·385**	**4·403**	**4·421**	**4·439**
54	0·227$_6$	0·227$_7$	0·225$_9$	0·225	0·224$_1$	0·223$_2$	0·222$_4$	0·221$_5$	0·220$_6$	0·219$_8$
	4·457	**4·476**	**4·494**	**4·512**	**4·531**	**4·549**	**4·568**	**4·587**	**4·606**	**4·624**
55	0·218$_9$	0·218$_1$	0·217$_2$	0·216$_4$	0·215$_5$	0·214$_7$	0·213$_8$	0·213	0·212$_2$	0·211$_4$
	4·643	**4·662**	**4·682**	**4·701**	**4·720**	**4·739**	**4·759**	**4·778**	**4·798**	**4·817**
56	0·210$_5$	0·209$_7$	0·208$_9$	0·208$_1$	0·207$_3$	0·206$_5$	0·205$_6$	0·204$_8$	0·204	0·203
	4·837	**4·857**	**4·877**	**4·897**	**4·917**	**4·937**	**4·957**	**4·977**	**4·998**	**5·018**
57	0·202$_4$	0·201$_7$	0·200$_9$	0·200$_1$	0·199$_3$	0·198$_5$	0·197$_7$	0·197	0·196$_2$	0·195$_4$
	5·039	**5·059**	**5·070**	**5·101**	**5·122**	**5·142**	**5·163**	**5·185**	**5·206**	**5·227**
58	0·194$_7$	0·193$_9$	0·193$_1$	0·192$_4$	0·191$_6$	0·190$_9$	0·190$_1$	0·189$_4$	0·188$_6$	0·187$_9$
	5·248	**5·270**	**5·291**	**5·313**	**5·334**	**5·356**	**5·378**	**5·400**	**5·422**	**5·444**
59	0·187$_2$	0·186$_4$	0·185$_7$	0·185	0·184$_3$	0·183$_5$	0·182$_8$	0·182$_1$	0·181$_4$	0·180$_7$
	5·466	**5·489**	**5·511**	**5·533**	**5·556**	**5·578**	**5·601**	**5·624**	**5·647**	**5·670**
60	0·180	0·179$_3$	0·178$_6$	0·177$_9$	0·177$_1$	0·176$_4$	0·175$_8$	0·175$_1$	0·174$_4$	0·173$_7$
	5·693	**5·716**	**5·739**	**5·763**	**5·786**	**5·810**	**5·833**	**5·857**	**5·881**	**5·905**
61	0·173	0·172$_3$	0·171$_6$	0·171	0·170$_3$	0·169$_6$	0·169	0·168$_3$	0·167$_6$	0·167
	5·929	**5·953**	**5·977**	**6·001**	**6·026**	**6·050**	**6·075**	**6·099**	**6·124**	**6·149**
62	0·166$_3$	0·165$_7$	0·165	0·164$_4$	0·163$_7$	0·163$_1$	0·162$_4$	0·161$_8$	0·161$_2$	0·160$_5$
	6·174	**6·199**	**6·224**	**6·250**	**6·275**	**6·300**	**6·326**	**6·352**	**6·377**	**6·403**
63	0·159$_9$	0·159$_2$	0·158$_6$	0·158	0·157$_4$	0·156$_8$	0·156$_1$	0·155$_5$	0·154$_9$	0·154$_3$
	6·429	**6·455**	**6·482**	**6·508**	**6·534**	**6·561**	**6·587**	**6·614**	**6·641**	**6·668**
64	0·153$_7$	0·153$_1$	0·152$_5$	0·151$_9$	0·151$_3$	0·150$_7$	0·150$_1$	0·149$_5$	0·148$_9$	0·148$_3$
	6·695	**6·722**	**6·749**	**6·776**	**6·804**	**6·831**	**6·859**	**6·887**	**6·915**	**6·943**
65	0·147$_7$	0·147$_1$	0·146$_6$	0·146	0·145$_4$	0·144$_8$	0·144	0·143$_7$	0·143$_1$	0·142$_6$
	6·971	**6·999**	**7·027**	**7·056**	**7·084**	**7·113**	**7·142**	**7·171**	**7·200**	**7·229**
66	0·142	0·141$_4$	0·140$_9$	0·140$_3$	0·139$_8$	0·139$_2$	0·138$_7$	0·138$_1$	0·137$_6$	0·137
	7·258	**7·288**	**7·317**	**7·347**	**7·376**	**7·406**	**7·436**	**7·466**	**7·496**	**7·527**
67	0·136$_5$	0·135$_9$	0·135$_4$	0·134$_9$	0·134$_3$	0·133$_8$	0·133$_3$	0·132$_7$	0·132$_2$	0·131$_7$
	7·557	**7·588**	**7·618**	**7·649**	**7·680**	**7·711**	**7·742**	**7·774**	**7·805**	**7·837**
68	0·131$_2$	0·130$_7$	0·130$_1$	0·129$_6$	0·129$_1$	0·128$_6$	0·128$_1$	0·127$_6$	0·127$_1$	0·126$_6$
	7·868	**7·900**	**7·932**	**7·964**	**7·996**	**8·028**	**8·061**	**8·093**	**8·126**	**8·159**
69	0·126$_1$	0·125$_6$	0·125$_1$	0·124$_6$	0·124$_1$	0·123$_6$	0·123$_1$	0·122$_6$	0·122$_1$	0·121$_7$
	8·192	**8·225**	**8·258**	**8·292**	**8·325**	**8·359**	**8·392**	**8·426**	**8·461**	**8·494**
70	0·121$_2$	0·120$_7$	0·120$_3$	0·119$_8$	0·119$_3$	0·118$_9$	0·118$_4$	0·117$_9$	0·117$_4$	0·116$_9$
	8·529	**8·563**	**8·598**	**8·633**	**8·667**	**8·702**	**8·737**	**8·772**	**8·808**	**8·843**
71	0·116$_5$	0·116	0·115$_5$	0·115$_1$	0·114$_6$	0·114$_2$	0·113$_7$	0·113$_3$	0·112$_8$	0·112$_4$
	8·879	**8·915**	**8·951**	**8·987**	**9·023**	**9·059**	**9·096**	**9·133**	**9·170**	**9·207**
72	0·111$_9$	0·111$_5$	0·111	0·111$_6$	0·110$_2$	0·109$_7$	0·109$_3$	0·108$_9$	0·108$_4$	0·108
	9·244	**9·281**	**9·318**	**9·356**	**9·394**	**9·431**	**9·470**	**9·508**	**9·546**	**9·584**

In most of what follows, S is treated as constant during the course of any one titration, and the approximation in this form seems to be justified by experiment (see Section 11), but this point is further discussed in Section 13.

3. Equation (7) may be regarded as a substituted form of (8), where

$$X = Mn/2S(V_e - M) = Mn/2SV \quad . \quad . \quad . \quad (10)$$

$$U = F(E - E_e)/RT = 0{\cdot}04(E - E_e)_{17^\circ} \quad . \quad . \quad (11)$$

so that X represents the amount of reagent required, expressed in terms of the unit $2SV/n$, whilst U represents the potential of the electrode reckoned from the end-point and in terms of the unit RT/F (which is just 25 millivolts at 17°). Similarly for an *earlier* stage (M', V', E', as in Part 1),

$$X' = X + x = \sinh(U + u) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where $$X' = M'n/2S(V_e - M') = M'n/2SV' \quad . \quad . \quad (13)$$

$$U + u = F(E' - E_e)/RT = F(E - E_e + \varepsilon)/RT \quad . \quad (14)$$

and, for the differences, x and u,

$$u = F\varepsilon/RT = 0{\cdot}04\,\varepsilon_{17^\circ} \quad . \quad . \quad . \quad . \quad (15)$$

$$\text{and } x = mnV_e/2SVV' = mn(1 + M/V)/2SV' \quad . \quad . \quad (16)$$

which (when M/V is negligible) becomes

$$x \approx mn/2SV' \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

so that u is the potential change in terms of the unit RT/F and is virtually an experimental quantity ($0{\cdot}04\,\varepsilon_{17^\circ}$), whilst x is the corresponding addition of reagent expressed in terms of the unit $2SVV'/nV_e(\approx 2SV'/n)$, and is known, at least approximately, if S is known. For the precise evaluation of x when M/V is not negligible, a rough estimate of M is required (see Section 5). Finally, if $r = X/x$,

$$r = MV'/mV_e = M(V - m)/m(V + M) \quad . \quad . \quad (18)$$

or

$$M = rm/[1 - m(1 + r)/V] \text{ [compare Part I, equation (30)]} \quad (19)$$

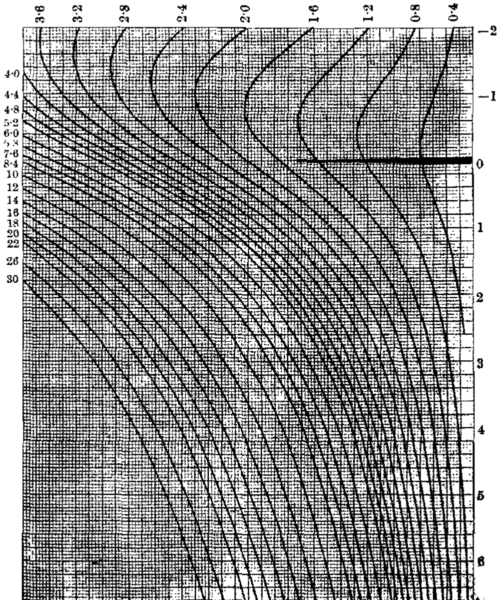
$$\approx rm(1 + m/V) \text{(when } m/V \text{ is small)} \quad . \quad . \quad (20)$$

Thus M, and therefore the result of the titration, is obtainable from the ratio r without knowledge of S. It is alternatively obtainable from X if S is known [see (10)].

4. ***Method II. Refined Method*** (S *known*).—In Fig. 1, X is represented graphically as a function of x and ε_{17° ($=25\,u$). In a somewhat different manner, Fig. 2 represents the ratio r as a function of the same quantities, the curves being curves of constant r (The experimental values of x and ε_{17° fix a point on this diagram whose position on the scale formed by the curves gives the value

of r.) In this way Method 1 is extended to and beyond the end-point, provided x is known, *i.e.*, provided S is known.

FIG. 1.



Curves of constant x, the value of x being given by the number at the right-hand end of each curve; x is a quantity of reagent added, expressed in terms of the unit $2SVV'/nV_s (\simeq 2SV'/n)$. Ordinates represent the resulting potential change ϵ_{17° (roughly corrected to 17°) in millivolts, and abscissæ the further amount (X) of reagent *still required to reach the end-point* ($X = 0$), expressed in terms of the unit $2SV/n$. For a given value of x, the corresponding curve (interpolated if necessary) enables the distance (X) from the end-point to be deduced from the potential change observed.

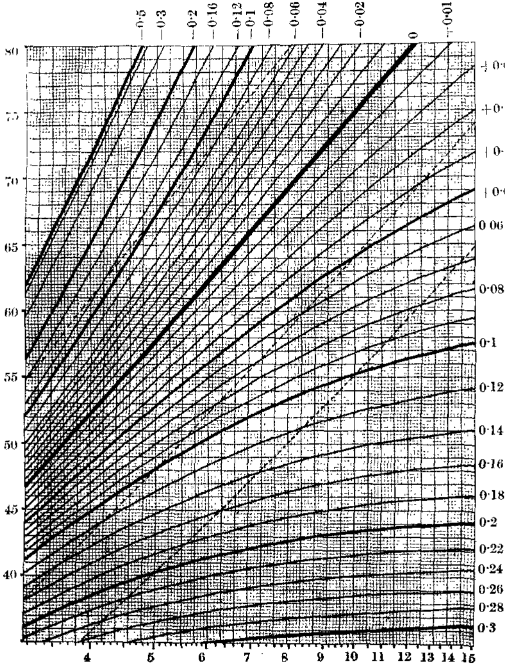
The functions represented in Figs. 1 and 2, *viz.*,

$$X = \pm \tfrac{1}{2}[x^2 \coth^2 u/2 - 4 \cosh^2 u/2]^{\frac{1}{2}} - x/2 \quad . \quad (21)$$

and the same divided through by x, are not convenient for the purpose of calculation, but by means of the relation

$$\operatorname{sech}(U + u/2) = (\sinh u/2)/\tfrac{1}{2}x \quad . \quad . \quad . \quad (22)$$

Fig. 2.



Curves of constant r, forming a numbered scale, the value of r being givei at the right-hand end of each curve. Abscissæ are proportional to $\log_{10} x$ which ranges from 0·5 to 1·18, but a numbered scale of x is provided. Ordinates represent ϵ_{17°.

obtained from (7) and (12), U, and therefore x, is easily obtained. Conveniently, the substituted form (in millivolts)

$$\text{sech}\,[0{\cdot}04\{(E - E_e)_{17^\circ} + \tfrac{1}{2}\varepsilon_{17^\circ}\}] = \sinh\,[0{\cdot}04(\tfrac{1}{2}\varepsilon_{17^\circ})]/\tfrac{1}{2}x \quad . \quad (22a)$$

may be employed with the aid of Table I, which contains a useful range of values of the hyperbolic sine and secant, tabulated in parallel against 25 times the argument, so that sinh u and sech u, for instance, are to be found (in heavy and ordinary type, respectively) against ε_{17°. sinh $\frac{1}{2}u$ is first found (against $\frac{1}{2}\varepsilon_{17^\circ}$) and divided by $\frac{1}{2}x$, and the quotient, which is sech $(U + \frac{1}{2}u)$, is sought in the body of the table (figures in ordinary type). Then on moving back $\frac{1}{2}\varepsilon_{17^\circ}$ millivolts in the table, sinh U, which is X, is found in the figures in heavy type.

This is the most exact form of the method, but the accuracy of the diagrams, particularly of Fig. 2, is in most cases as great as is justified by the precision with which x and ε are known.

5. There is theoretically an ambiguity in the determination, as may be seen from the symmetry of the curves in Fig. 1, or the alternative signs in equation (21). The found values of X and r might, in reality, be the values of $-(X + x)$, and $-(r + 1)$, respectively: but this would mean that the end-point had been overstepped by a very large amount, *viz.*, *more* than $\frac{1}{2}x$, and in practice the doubt will not arise, because an approximate determination will already have been made by Method I (see examples, Section 11). The latter will also enable the small correction $Mmn/2SV'V$, by which the exact form of x differs from the approximate form $mn/2SV'$, to be applied with sufficient precision (it is often negligible). The result of the titration (M_0), as determined by Method II, depends upon (*a*) the quantities ($M_0 - M$), m, V, and n, which may be regarded as accurately known; (*b*) the measured potential change ε, in which there is an absolute uncertainty dependent on the behaviour of the electrodes (Part I, Section 3); and (*c*) the assumed value of S.

Supposing S to be correctly known, it is clear that for a given absolute error in ε_{17°, the precision of the result, in terms of concentration, will be proportional to the absolute sensitivity of ε_{17° to change in X, *i.e.*, to the steepness of the curve in Fig. 1 at the point from which the reading would be taken. It can be shown that this sensitivity (the tangent of slope of these curves, in millivolts per unit of X) is $25[\text{sech}\,U - \text{sech}(U + u)]$, which has a maximum value of 25 when $X = 0$ and x is infinite; but Fig. 1 shows that this theoretical maximum sensitivity can be closely approached if X is small and x fairly large, *i.e.*, if the final measurement of the potential of the electrode is made within about $\frac{1}{4}$ unit

(*of reagent*) *of the end-point*, and x is reckoned from a stage at least 5 or 6 units earlier.

An equally sensitive potential change occurs *after the end-point has been passed, viz.*, between two stages, of which one is within ½ unit of the end-point, and the other is at least 5 or 6 units later. This is the "ambiguous" case already mentioned. (*This depends upon the use of the second half of the titration curve;* but *see Section 7.*)

The prior use of Method I (upon the same sample of solution) enables these conditions to be fulfilled in a single titration. In this way, with ε defined to within $\pm$ 0·5 millivolt (compare Part I), the absolute uncertainty of the result of the titration can be reduced to little more than $\pm$ 0·02 unit (in terms of concentration $\pm$ 0·04S), provided S is known correctly. The *probable* error can be further reduced by making several potential measurements near the end-point, using them for independent calculations of M_0, and averaging the results.

6. Error in the assumed value of S, on the other hand, will have a one-way effect, not to be reduced by averaging. It will produce an equal relative error in x, whose effect on the result can be gauged by means of Fig. 2. In this diagram the curves are lines of constant r, and from r the result of the titration follows without reference to S. The abscissæ are proportional to $\log x$, one large square representing a change of about 5% in x, so that an error of 5% in the assumed value of S will produce an error of one large square in the abscissa of the representative point. It follows that the slope of these curves represents the error in ε which would just cancel an error of 5% in S. The effect of the possible error in S is thus obtained as an equivalent error in ε, which should of course be kept smaller than the experimental uncertainty in ε. In the diagram three dotted lines of constant X have been inserted, *viz.*, $X = 1$, $X = 0·5$, and $X = -0·5$ (they are roughly parallel to the line $X = r = 0$), and it is seen that the error in ε which is equivalent to a 5% error in S is about 0·35 millivolt when $X = 1$, nearly 0·7 millivolt when $X = 0·5$, and about 1·25 millivolts at the end-point, while at half a unit past the end-point (when $X = -0·5$) it is about 1·8 millivolts.

Thus on approaching within ½ unit of the end-point with the object of obtaining the highest sensitivity in ε, it is necessary to know the value of S within $\pm$ 2%; and when the uncertainty in S is appreciably greater than this, the best result is obtained by not approaching the end-point so closely.

7. This method depends upon the experimental realisation of only one-half of the titration curve expressed by equation (8).

It is applicable, for instance, to acidimetry with a quinhydrone electrode, and in the presence of carbon dioxide. Its main disadvantage is the necessity for fairly precise knowledge of the constant S, in order to obtain the highest precision. When, as in the case of the silver-chloride titration for example, the whole of the titration curve conforms to equation (8), a method becomes available which is free from this disadvantage, no knowledge of S being required.

8. *Method III. Refined Method* (S *unknown*).—This depends upon the measurement of two successive potential changes, ϵ and ϵ', corresponding to two successive additions of reagent, m and m' c.c.; from these four quantities, together with the approximate volume of the solution at the intermediate stage, the result of the titration is calculated, without either assuming or determining the value of S. Thus three stages are involved, the two already considered (M', V', E', and M, V, E) to which equations (12) and (7) correspond, and a later stage ($M + m$, $V + m$, $E - \epsilon'$), for which a similar equation may be written, *viz.*,

$$X - x = \sinh (U - u') \quad . \quad . \quad . \quad . \quad (23)$$

so that $u' = F\epsilon/RT = 0{\cdot}04\ \epsilon'_{17^\circ}$, and

$$x' = m'nV_e/2SV(V + m') \quad . \quad . \quad . \quad . \quad (24)$$

From equations (7) and (12), the relation

$$X/x = \tfrac{1}{2}[\tanh (U + \tfrac{1}{2}u) \coth \tfrac{1}{2}u - 1] \quad . \quad . \quad (25)$$

is derived, and from (7) and (23), similarly,

$$X/x' = \tfrac{1}{2}[\tanh (U - \tfrac{1}{2}u') \coth \tfrac{1}{2}u' + 1] \quad . \quad . \quad (26)$$

Between (25) and (26), U can be eliminated, giving

$$2X = (x \coth \tfrac{1}{2}\, u - x' \coth \tfrac{1}{2}\, u') \coth \tfrac{1}{2}\, (u + u') - (x - x') \quad . \quad (27)$$

By substituting for X, x, x', u, and u', making use of the function tabulated in Table I (Part I), and dividing throughout by nV_e/SV^2, one obtains

$$\frac{M}{1 + M/V} = \{1 + 2f(\epsilon + \epsilon')\}\left[\frac{m\,.f(\epsilon)}{1 - m/V} - \frac{m'\,.f(\epsilon')}{1 + m'/V}\right] + f(\epsilon + \epsilon')\left[\frac{m}{1 - m/V} - \frac{m'}{1 + m'/V}\right] \quad . \quad . \quad (28)$$

When the values of ϵ, ϵ', m, m', and the approximate value of V are inserted (from experiment) this equation reduces to a linear equation for M (which gives the result of the titration).

In practice ($\epsilon + \epsilon'$) is of the order of 100 millivolts or more, and m and m' are not large fractions of V, so approximation gives

$$M\ (\text{app.}) = m_c\,.f(\epsilon) - m_c'f(\epsilon') \quad . \quad . \quad . \quad (29)$$

where $m_c = m - m^2/V$, and $m_c' = m' - m'^2/V$. The small terms neglected in this approximation are almost exactly

$$\text{(Small terms)} \quad M^2\,(\text{app.})/V + [m^2/V^2 \,.\, m_c \,.\, f(\varepsilon) - m'^2/V^2 \,.\, m_c' \,.\, f(\varepsilon')] + f(\varepsilon + \varepsilon')[2M\,(\text{app.}) + (m_c - m_c')] \quad . \quad (30)$$

In the examples given in Section 11, these small terms are in each case roughly evaluated and added to the approximate result obtained by the use of (29), but, as may be seen, the correction is only of the same order of magnitude as the uncertainty of the result.

9. Alternatively a graphical method of calculation may be used. When divided throughout by $2x$, equation (27) gives (in terms of the function f)

$$r = X/c = [1 + 2f(\varepsilon + \varepsilon')][f(\varepsilon) - a \,.\, f(\varepsilon')] + f(\varepsilon + \varepsilon')[1 - a] \quad . \quad (31)$$

where $a = x'/x = m'(V - m)/m(V + m')$. This relation can be expressed graphically for any fixed value of a. Fig. 3 represents the case where $x' = x$, and

$$r = [1 + 2f(\varepsilon + \varepsilon')][f(\varepsilon) - f(\varepsilon')] \quad . \quad . \quad . \quad (32)$$

If the second addition of reagent (m') is made such that

$$m' = m/(1 - 2m/V) \quad . \quad . \quad . \quad . \quad . \quad (33)$$

the condition $x = x'$ is fulfilled, and the measured potential changes ε and ε' (corrected to 17°) then fix a point on this diagram, whose position on the scale formed by the curves gives the value of r; whence the result of the titration follows by equation (19) or (20).

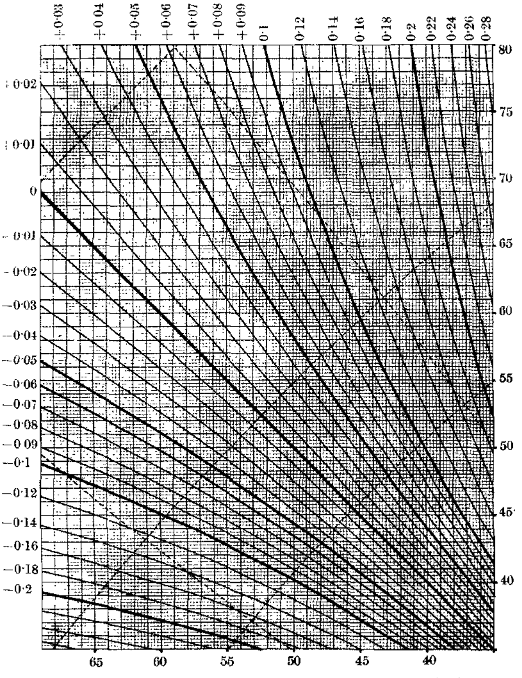
10. *Conditions for Precision of Method III.*—If the second of the three stages concerned is within ½ unit of the end-point (on either side of it), and the other two stages are at least 5 units earlier and later, respectively, both the potential changes will be of high sensitivity (see Section 5), and it is obvious that these are the conditions for high precision by this method (but see Section 13). Knowledge of the value of the constant S is not required, although a rough estimate of it is useful in arranging the conditions. It is really only necessary, however, that the intermediate stage should be as near as can be judged (by use of Method I) to the end-point, and that the two potential changes should be of the order of 50 millivolts or more.

11. *Results.*

Some examples of the application of Method III (chiefly) are recorded below. Apparatus and materials were essentially as in Part I, and the gradual fall of the potential of the quinhydrone electrode, due to dilution of the acid present by the added reagent, was allowed for by correcting the measured potentials to a constant

volume such as 100 or 1000 c.c. (according to Part I, Section 11). This correction is given under the heading " Corr."

FIG. 3.



Curves of constant *r*, forming a numbered scale (the value of *r* is given at the right-hand end of each curve). Subject to the condition that $x' = x$, *i.e.*, that $m' = m/(1 - 2m/V)$, the ordinate represents the first of the two successive potential changes ($\epsilon_{17°}$), and the abscissa the second ($\epsilon'_{17°}$), and the position of the point so defined, on the scale of *r* formed by the curves, gives the value of *r*. The dotted lines are typical lines of constant X ($X = +0·5$ and $X = -0·5$) and of constant x ($x = 3$, 4, and 8).

Example 1. 1000 C.c. $N/1000$-KCl titrated by $N/100$-$AgNO_3$ (temp. $\approx$ 14·5°).

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/2000$.)

By Method I (see Part I, Section 10, Example 3) from stages 0, I, and II, the number (M) of c.c. of reagent still required at Stage II, is found to be about 13·7. Hence 13 c.c. are now added, and afterwards a further 12 c.c. (the unit $2SV'/n$ being roughly 2·5 c.c.); the corresponding potentials are measured (Stages III and IV) and (together with E_{II}) corrected (a) to 17° by addition of the small correction, $E/120$ (see Part I, Section 5), and (b) to 1000 c.c. volume as regards the quinhydrone electrode.

Stage.	$M_0 - M$.	$\frac{M_0 - M}{1000}$	Corr.	E (expt.)	$E_{17°}$.	E (corr.)
II	85	0·085	2·0	172·2	173·6	175·6
III	98	0·098	2·3	118·1	119·1	121·4
IV	110	0·110	2·6	58·3	58·8	61·4

Then from the potential changes, ε and ε' (Stages II—III and III—IV, respectively), and the corresponding additions of reagent, m and m', together with the approximate volume $V(= 1100$ at Stage III), the amount of reagent still required at Stage III [M (app.)] is calculated by equation (29), and so by addition of $(M_0 - M)$, which is 98 at Stage III, the result M_0 (app.) is obtained. The small terms are then approximately evaluated by the formula (30) and added, to obtain the final M_0.

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	m_ϵ.	$m_\epsilon . f(\epsilon)$.	$m^2/V^2 . m_\epsilon . f(\epsilon)$.
II—III	54·2	0·1292	13	+0·15	13·15	1·699	0·0002
III—IV	60·0	0·0998	12	−0·13	11·87	1·185	0·0001
	$f(\epsilon + \epsilon') = 0·0105$			$(m_\epsilon - m'_\epsilon) =$	1·28	M (app.) $= 0·51_5$ M_0 (app.) $= 98·51_5$	Diff. = 0·0001

Small terms : $\{0·0003 + 0·0001 + 0·0105[2 \times 0·515 + 1·28]\} \approx 0·025$.

$M_0 = 98·54$. Error = +0·04%

Example 2. 100 C.c. $N/1000$-KCl titrated by $N/1000$-$AgNO_3$ (temp. $\approx$ 20°).

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than $N/4000$.)

By Method I (see Part I, Example 4) the amount of reagen still required at Stage II is found to be about 24 c.c.; 21 c.c. ar added (the unit $2SV/n$ being roughly 5 c.c.) followed by 4 c. and then a further 25 c.c., the corresponding potentials (Stages II IV, and V) being measured, and corrections being made to 17° ar 100 c.c.

Stage.	$M_0 - M$.	$\frac{M_0 - M}{100}$.	Corr.	E (expt.)	E_{17°.	E (corr.)
II	75	0·75	14·0	190·4	188·5	202·5
III	96	0·96	16·8	139·8	138·4	155·2
IV	100	1·0	17·3	120·5	119·3	136·6
V	125	1·25	20·3	68·4	67·7	88·0

Two independent calculations are now made, from Stages II—III—V and from Stages II—IV—V, respectively, each as in Example 1, and the results averaged.

(*a*) From Stages II, III, and V. $V = 196$ (Stage III).

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	m_e.	$m_e . f(\epsilon)$.	$m^2/V^2 . m_e . f(\epsilon)$.
II—III	47·3	0·1776	21	+2·25	23·25	4·13	$0·047_6$
III—V	67·2	0·0730	20	−4·20	24·71	$1·80_4$	$0·039_5$
	$f(\epsilon + \epsilon') = 0·0104$		$(m_e - m'_e) = -1·46$			M (app.) $= 2·32_2$; M_0 (app.) $= 98·32_2$	Diff. = 0·008

Small terms: $[0·028 + 0·008 + 0·0104\{2 \times 2·33 - 1·46\}] \approx 0·069$

$M_0 = 98·39_1$. Error = −0·11%.

(*b*) From Stages II, IV, and V. $V = 200$ (Stage IV).

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	m_e.	$m_e . f(\epsilon)$.	$m^2/V^2 . m_e . f(\epsilon)$.
II—IV	65·9	0·0772	25	+3·13	28·13	$2·17_1$	0·034
IV—V	48·6	0·1671	25	−3·13	21·87	$3·65_5$	0·057
	$f(\epsilon + \epsilon') = 0·0104$		$(m_e - m'_e) = 6·26$			M (app.) $= -1·48_4$; M_0 (app.) $= 98·51_6$	Diff. = −0·023

Small terms: $\{0·011 - 0·023 + 0·0104[2 \times (-1·48) + 6·26]\} \approx 0·02_2$

$M_0 = 98·54$. Error = +0·04%.

Mean result from (*a*) and (*b*): M_0 (mean) = 98·47. Error = −0·03%.

Example 3. 1000 C.c. N/10,000-KCl titrated by N/1000-$AgNO_3$ (*temp.* $\approx 17°$).

(Actually known to be equivalent to 98·5 c.c. of $AgNO_3$, but titrated as if only known to be stronger than N/15,000.)

The unit $2SV/n$ being approximately 25 c.c., Method I is inapplicable from the commencement, the end-point being too near. The *first approximation is therefore obtained by Method II, on the assumption that the unit is about* 25 c.c.; 15 c.c. of reagent are added and the initial potential is measured. Then 50 c.c. (2 units) more are added and the second potential is measured. The potentials are corrected to 1000 c.c. as regards the quinhydrone electrode, and subtracted. From the curve, $x = 2$ (Fig. 1), the value of X corresponding to the change of potential (ϵ) is read, and multiplied by 25, thus giving M (app.).

Stage.	$M_0 - M$.	$\frac{M_0 - M}{1000}$.	Corr.	E (expt.).	E (corr.).	ϵ.	m.	x.	x'.	M (app.).
0	15	0·015	0·4	167·9	168·3					
I	65	0·065	1·6	145·5	147·1	21·2	50	2	1·25	31·3

Addition of the correction ($MM'/V' \approx 2·5$) for change in the unit gives $M = 33·8$, $M_0 = 98·8$.

Assuming, therefore, that about 34 c.c. of reagent are still required at Stage II, one adds, first, 25 c.c., then successively 10 c.c., 10 c.c.,

and 100 c.c., measuring the four corresponding potentials and correcting as before.

Stage.	$M_0 - M$.	$\frac{M_0 - M}{1000}$.	Corr.	E (expt.).	E (corr.).
II	90	0·09	2·2	126·0	128·2
III	100	0·10	2·4	116·1	118·5
IV	110	0·11	2·6	107·2	109·8
V	210	0·21	4·8	64·0	68·8

Then three calculations are made (from 0—II—V, from 0—III—V, and from 0—IV—V, respectively), each as in Example 1, and the results averaged.

(*a*) From Stages 0, II, and V. $V = 1090$ (Stage II).

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	$m\epsilon$.	$m\epsilon \cdot f(\epsilon)$.	$m^2/V^2 \cdot m\epsilon f(\epsilon)$
0—II	40·1	0·2517	75	+ 5·16	80·16	20·18	0·10
II—V	59·4	0·1025	120	−13·21	106·79	10·95	0·13
	$f(\epsilon + \epsilon') = 0{\cdot}019$		$(m\epsilon - m'\epsilon) = -26{\cdot}6$			M (app.) $= 9{\cdot}23$ M_0 (app.) $= 99{\cdot}2_5$	Diff. $= -0{\cdot}03$

Small terms : $\{0{\cdot}08 - 0{\cdot}03 + 0{\cdot}019[2 \times 9{\cdot}2 - 26{\cdot}6]\} \approx -0{\cdot}11$

$M_0 = 99{\cdot}1$. Error $= +0{\cdot}06\%$.

(*b*) From Stages 0, III, and V. $V = 1100$ (Stage III).

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	$m\epsilon$.	$m\epsilon \cdot f(\epsilon)$.	$m^2/V^2 \cdot m\epsilon f(\epsilon)$
0—III	49·8	0·1585	85	+ 6·57	91·57	14·51	0·09
III—V	49·7	0·1587	110	−11·00	99·00	15·71	0·16
	$f(\epsilon + \epsilon') = 0{\cdot}010$		$(m\epsilon - m'\epsilon) = -7{\cdot}4$			M (app.) $= -1{\cdot}2$ M_0 (app.) $= 98{\cdot}8$	Diff. $= -0{\cdot}07$

Small terms : $\{0{\cdot}00 - 0{\cdot}07 + 0{\cdot}019[2 \times (-1{\cdot}2) - 7{\cdot}4]\} \approx -0{\cdot}26$

$M_0 = 98{\cdot}5_4$. Error $= +0{\cdot}04$°

(*c*) From Stages 0, IV, and V. $V = 1110$ (Stage IV).

Stages.	ϵ.	$f(\epsilon)$.	m.	$\pm m^2/V$.	$m\epsilon$.	$m\epsilon \cdot f(\epsilon)$.	$m^2/V^2 \cdot m\epsilon f(\epsilon)$
0—IV	58·5	0·1066	95	+8·13	103·13	10·99	0·08
IV—V	41·0	0·2407	100	−9·01	90·99	21·90	0·18
	$f(\epsilon + \epsilon') = 0{\cdot}019$		$(m\epsilon - m'\epsilon) = +12{\cdot}1$			M (app.) $= -10{\cdot}9_1$ M_0 (app.) $= 99{\cdot}0_9$	Diff. $= -0{\cdot}10$

Small terms : $\{0{\cdot}11 - 0{\cdot}10 + 0{\cdot}019[2 \times (-10{\cdot}9) + 12{\cdot}1]\} \approx -0{\cdot}17$

$M_0 = 98{\cdot}9_2$. Error $= +0{\cdot}4_9$

Mean result from (*a*), (*b*), and (*c*) : M_0 (mean) $= 98{\cdot}8_5$. Error $= +0{\cdot}3_5\%$.

12. *Determination of the End-point Potential, and of the Consta* S.—The result of the titration is obtained without calculati either of these quantities. Both, however, may be calculated frc the measurements if they are of interest, and this is probably t most exact method of determining them. Various formulæ mig be given for the calculation of E_e. For instance from equati (25) the relation

$$f[\varepsilon_{17^\circ} + 2(E - E_e)_{17^\circ}] = [f(\varepsilon) - r]/(1 + 2r) \quad . \quad (34$$

or, alternatively,

$$f(2E - 2E_e)_{17^\circ} = [1 + f(\varepsilon_{17^\circ})][f(\varepsilon_{17^\circ})/r - 1]/[1 + 2f(\varepsilon_{17^\circ})] \quad (34a$$

is obtained, which enables E_e to be evaluated by means of Tabl (Part I), the value of r being obtained either directly by equat (31), or from the result of the titration and equation (19).

When E_c is known, U is known, and S can then be calculated by the formula

$$2S = \frac{n(m + m')}{(V - m) \sinh (u + U) + (V + m') \sinh (u' - U)} \quad (35)$$

$$= \frac{n(m + m')}{(V - m) \sinh [0{\cdot}04\{\varepsilon_{17^\circ} + (E - E_c)_{17^\circ}\}] + (V + m') \sinh [0{\cdot}04\{\varepsilon'_{17^\circ} - (E - E_c)_{17^\circ}\}]} \quad (36)$$

the hyperbolic sines being obtained from Table I (this Part).

The precise measurement of E_c under standard conditions is of interest in connexion with "absolute" methods of potentiometric titration (see Part I and previous paper, *loc. cit.*), whilst the value of S is required in Method II, described above.

13. *Precision of Method III, and Dependence on the Constancy of* S.—Analytically the small error (dM) in M due to small errors, du and du', in u and u', can be estimated by the equation

$$\frac{n}{2SV} \cdot dM = \frac{p \cdot du' - du}{\Delta \text{ sech } U + p\Delta' \text{ sech } U} \quad . \quad . \quad . \quad (37)$$

where Δ sech U and Δ' sech U represent [sech U – (V/V') sech $(U + u)$] and [sech U – $V/(V + m')$. sech $(U - u)$] respectively, and

$$p = [\tanh (U + u) - \tanh U]/[\tanh U - \tanh (U - u)].$$

Thus p represents the relative importance of equal errors in u and u' (p is also the expression for the slope of the curves in Fig. 3). The conditions for high precision are easily deduced from equation (37). Under the ideal conditions ($X = 0$ and both x and x' are infinite), it reduces to $(n/2SV) \cdot dM = \frac{1}{2} (du' - du)$, showing that (under these conditions) equal errors in u and u' will cancel if in the same direction, and if in opposite directions will have the same effect as a single error of the same magnitude as either in u in Method II. Thus the minimum absolute uncertainty is the same as for Method II, but the probable error is less, and also the precision is not dependent on knowledge of S.

With regard to the effect of slight variation of S during the course of a titration, it can be shown that if it changes by 1% between the first and second of the three stages the effect will be equivalent to an error of about 0·25 millivolt in the first potential change (ε); and similarly as between the second and third stages. The effects on the result are in the same direction when the variations in S are in the same direction.

Summary.

The methods described depend on the changes of the potential of the indicator-electrode, not on the particular values of the potential. Method I (see Part I) is applicable in all ordinary

cases, where an absolute uncertainty of the order of one-fifth or one-seventh of the solubility of silver chloride (or the corresponding constant) is permissible. A first tentative addition of reagent is made, and from the resulting potential change an approximate estimate of the amount still required is obtained by the use of Table I. Nearly this amount is then added, and the small residual deficiency is precisely evaluated by the same means. Precision depends chiefly on the closeness of approach to the end-point, which in the most dilute solutions is limited by the incompleteness of the reaction (which would invalidate the method) in the neighbourhood of the end-point.

The other two methods (Part II), essentially for very dilut solutions, are of a somewhat higher order of absolute precision Method II is the extension of Method I to and beyond the end point, depending upon fairly precise knowledge of the constant S (the solubility of silver chloride in the solution), and the use eithe of a set of accurately drawn curves (Figs. 1 and 2) or of a numerica table (Table I, Part II).

Method III is independent of knowledge of the constant S. Fro the two potential changes produced by two successive additior of reagent, the result of the titration is accurately obtained, eith by a simple calculation with the aid of Table I or by the use of set of curves (Fig. 3).

Methods II and III depend upon the conformity of the titratic curve (on one side of the end-point, for Method II; on both sid for Method III) to a slightly simplified form of a general equatic (Part II, Section 1) deduced (on the assumption of a reversit electrode) on thermodynamic grounds only.

Thanks are due to the Trustees of the Brunner Mond Resear Fund out of which the cost of apparatus used in this research w defrayed.

THE UNIVERSITY OF MANCHESTER. [*Received, October 29th, 1927.*]

CXVII.—*Autoxidation during Slow Combustion.*

By ERNEST WALTER JOHN MARDLES.

THE work carried out during 1925 in this laboratory include study of fuel detonation from the purely physical side (Callen and others, R. & M. No. 1013), which led to the conclusion tl the onset of detonation at high compression ratios, in the case liquid fuels, was due to the persistence of nuclear drops or resid of low ignition point, forming a relatively small percentage of

charge. The remarkable effect of very small quantities of organo-metallic compounds, such as lead tetraethyl and iron or nickel carbonyl, was attributed to the reducing action of the metal, which became concentrated in the nuclear residues, thus delaying their ignition.

A further study of the phenomena of slow combustion from the chemical side (Aeronautical Research Committee, R. & M. No. 1062, 1926; *Engineering*, Feb. 4th, 1927) confirmed these conclusions by showing that such nuclei in the form of fog and dew always preceded or accompanied the initial stage of oxidation. Analysis of the products of the reaction revealed traces of active oxygen, which became much more marked when the fuel was injected in the form of a fine spray, indicating the formation in the nuclear drops of some explosive organic peroxide, which would naturally account for their simultaneous ignition. The addition of lead tetraethyl to the fuel under these conditions completely changed the course of the reaction, inhibiting the appearance of active oxygen in the products, and raising the temperature of spontaneous ignition of the mixture.

Further experimental evidence has since been obtained in support of these conclusions, which helps to clear up some of the difficulties of the subject, and to answer most of the objections which have been raised against the theory of autoxidation.

Experimental.

Several independent methods have been employed, the most important of which will be referred to for brevity as (*a*) the tube method, (*b*) the bulh method.

(*a*) The tube method has been described fully (Callendar and others, *loc. cit.*) and was devised primarily with the view of identifying the products of reactions occurring in a fuel–air mixture when passed through a heated tube at any desired temperature. (*b*) In the bulb method, the mixture was heated in a closed bulb in order to obtain supplementary evidence with regard to the rate of reaction as the temperature was slowly raised. In both (*a*) and (*b*), the apparatus was duplicated and arranged differentially with a pair of tubes or bulbs heated under identical conditions, in order to observe more accurately differences of behaviour between different mixtures and changes induced by the addition of small quantities of oxidising or reducing agents.

(*a*) *The Tube Method.*

Some of the results of this method will be briefly summarised before proceeding to particular cases. The temperature of the

furnace, which was varied from about 150° to 700° as required, could be observed at any time with a platinum thermometer inserted in one of the experimental tubes. The temperature at which any action became observable was usually recorded as the *temperature of initial combustion*, though the reaction indicated was often quite different from that of complete combustion in a flame. The *temperature of inflammation*—that at which each mixture caught fire—could also be observed with considerable accuracy. The products of the initial reaction were accompanied by a fine and very persistent fog, which passed through all the reagents without absorption. This tended to confirm the nuclear origin of the reaction, but the products isolated were comparatively stable, familiar substances, such as aldehydes and acids, which were found to have no appreciable effect on detonation in an engine. It was concluded that these were final products of decomposition of some more active and unstable compounds, the search for which resulted in the discovery of the presence of active oxygen, presumably in the form of organic peroxides.

Additional Experiments. Tube Method.—(1) *Oxidation of hexane.* The hot gases from hexane–air mixtures were passed directly into slightly acidified potassium iodide solution, and the liberated iodine was titrated with *N*/50-sodium thiosulphate solution. There was only a very small quantity of "active" oxygen present when the gas mixture passing through the tube was heated longer than 1 minute, especially at higher temperatures. With decreasing times of heating, much larger yields were obtained, especially when the mixture was not completely vaporised but was introduced in the form of a fine spray containing minute drops of liquid. This is illustrated in Fig. 1, the values being calculated for 1 g. of hexane consumed (mixture strength about 12%).

In a further attempt to isolate the peroxides, a condenser made of German silver, through which cold water circulated, was inserted into the exit end of the tube heated in a vertical position. The condensate when concentrated in a vacuum left a gummy residue, which did not detonate on heating, but consisted merely of decomposition products. It would thus appear that the life of the primary peroxides (addition products of the fuel with oxygen molecules) is exceedingly short on account of their thermal instability and reactivity.

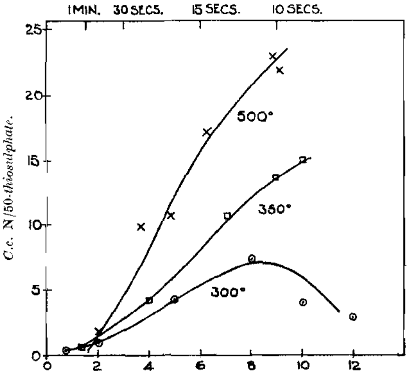
Staudinger (*Ber.*, 1925, **58**, 1075), who was unable to isolate primary peroxides, used the term "peroxide" for compounds of known structure and the name "moloxide" when the structure of the primary autoxidation product was not known or when the product could not be isolated. He considered that the moloxides

are very rich in energy and too unstable to permit of isolation. The peroxides he succeeded in isolating were violent explosives; for instance, the small amounts clinging to the walls of the container were often sufficient to shatter the vessel.

Legler (*Ber.*, 1885, **18**, 3343) isolated an organic peroxide, which exploded as violently as benzenediazonium nitrate, from the slow combustion products of ethyl ether in air, by concentrating the liquid obtained by condensation. However, this organic peroxide was of smaller molecular weight than the primary peroxide known to be formed from the oxidation of ether in air.

FIG. 1.

Time of heating.



Rate of passage of gas mixture through tube (litres per hour).

(2) *Autoxidation of benzene, aniline, etc., in presence of hexane.* When a small percentage of alcohol or benzene was added to the hexane, the yield of "active" oxygen was decreased. Other substances had a similar effect, reaching a maximum with iron carbonyl and lead tetraethyl. Some qualitative results are given in Table I for a 15% hexane–air mixture at temperatures below 400° (time of heating, about 25 secs.).

A similar reduction of "active" oxygen was observed when phenol or aniline was added to ether vapour mixed with air.

It was also found that a decrease in yield of aldehydes occurred,

TABLE I.

Substance added to hexane vapour, and approximate proportion.		*Effect on amount of "active" oxygen produced.*
Ethyl alcohol	5%	Marked decrease.
n-Butyl alcohol	2%	Slight ,,
Benzene and toluene	5%	*Moderate* ,,
Aniline	2%	Marked ,,
Phenol and *m*-cresol	—	,, ,,
Carbon monoxide	10%	None observed.
Lead tetraethyl	0·2%	,, ,,
Iron carbonyl	0·1%	,, ,,

especially with iron carbonyl and lead tetraethyl, indicating that peroxide and aldehyde formation were related. These results were obtained with a moderate time of heating and low temperature, no "active" oxygen being detected in the products of combustion of ethyl or butyl alcohol; with more rapid rates of heating and temperatures about 500—600°, a slight amount of "active" oxygen was obtained with ethyl alcohol and a larger amount with butyl alcohol, benzene, etc. (compare Bach, *Compt. rend.*, 1897, **124**, 951).

When benzene vapour was added to a hexane–air mixture and then passed through the hot tube at a temperature below 500° (at which the benzene vapour alone would remain unoxidised in air), autoxidation of the benzene occurred, since when bromine-water was added to the condensed products of slow combustion a small quantity of a white solid separated, m. p. 90°, which was identified as tribromophenol. An experiment was carried out to illustrate the autoxidation of aniline in the presence of hexane undergoing incipient oxidation. Three tubes were placed in the furnace kept at 350°, at which temperature aniline is relatively stable to oxidation. Through the first a hexane–air mixture was passed, through the second aniline vapour and air, and through the third a mixture of aniline and hexane vapour with air, the three tubes being arranged so that the conditions were as nearly as possible the same for all. After the mixtures had been passed for about 1 hour, the tube through which aniline and hexane vapour were passed contained a brown deposit on the walls, especially at the exit end of the tube and the other tubes were nearly clean. The condition of the dirty tube resembled that with aniline vapour–air at a temperature above 500° when oxidation of aniline is known to occur.

The removal of the "active" oxygen by aniline through autoxidation accounts at once for the anti-detonating action of this substance, but is not in agreement with the primary dehydrogenation theory of Lewis (J., 1927, 1555).

(3) *The influence of hydrogen peroxide on the combustion of hydrocarbons.* In the course of engine experiments at the Air Ministry Laboratory it was found that hydrogen peroxide solution adde

to the fuel behaved similarly to water (Table II). When a fine spray of water was injected into a hexane–air mixture passing through a heated glass tube, the temperature at which the aldehydes were first observed was several degrees higher than without the water. No ionisation was observed below 500°. With a concentrated hydrogen peroxide solution (60%) a similar effect was obtained, and again no ionisation could be detected. It is concluded that hydrogen peroxide does not autoxidise the combustion, and that any such effect previously obtained was due to the initial formation of much more active and unstable peroxides which could yield hydrogen peroxide by hydrolysis.

This conclusion accords with that established by the Traube–Hoppe Seyler discussion on the mechanism of autoxidation (*Ber.*, 1879, **12**, 1551; 1883, **16**, 117; 1889, **22**, 2215), *viz.*, that hydrogen peroxide is a relatively passive substance. Furthermore, the presence of hydrogen peroxide in the products of oxidation has long been known (compare Babo, *Jahresber.*, 1864, 135; Schönbein, *J. pr. Chem.*, 1866, 282, 258), and Clover (*J. Amer. Chem. Soc.*, 1922, **44**, 1107) emphasised the fact that hydrogen peroxide was not a primary product in the oxidation of ether, but one of decomposition.

TABLE II.

Effect of peroxides on the highest useful compression ratio (H.U.C.R.) of fuels determined in an E.35 variable-compression engine.

Fuel.	Observed H.U.C.R.
* 60/40 Ether–alcohol mixture	4·9
„ plus 5% (vol.) water	5·4
„ plus 5% (vol.) H_2O_2 solution (40 vol.)	5·2
Petrol mixture	4·9
„ plus 0·5% (weight) methyl ethyl ketone peroxide	4·2
„ plus 2·0% (weight) ethyl hydrogen peroxide	4·1

* Ethyl ether 60%, ethyl alcohol 40% (by vol.).

TABLE III.

The influence of hydrogen peroxide on temperature of ignition (liquid sprayed into tube).

Fuel.	Temp.
(*a*) Ethyl alcohol alone	570°
„ plus 10% (vol.) addition of water	575
„ plus 10% (vol.) H_2O_2 solution (60%)	570
(*b*) *n*-Butyl alcohol	545
„ plus 10% (vol.) water	559
„ plus 10% (vol.) H_2O_2 solution	560

Action of Organic Peroxides on the Self-ignition Temperature of Small Drops.

It was shown (Callendar, 1927) that the addition of lead tetraethyl to the spray of a hydrocarbon in air passing through a hot tube extinguished the flashes of flame, and that the addition of a detonation-inducing substance, such as *iso*amyl nitrite, lowered the self-ignition temperature.

Ormandy and Craven (*J. Inst. Pet. Tech.*, 1924, **10**, 335) found that lead tetraethyl apparently had little effect on the self-ignition temperature of petrol drops in the Moore apparatus, but further investigations relating to the self-ignition temperatures of organic vapours, and the effect of numerous anti-knock substances on these temperatures, have been carried out by a number of workers using the Moore method (Egerton and Gates, Aeronautical Research Committee, R. & M. No. 1079; *J. Inst. Pet. Tech.*, 1927, **13**, 244; Weerman, *ibid.*, p. 300; Tanaka and Nagai, *Proc. Imp. Acad. Tokio*, 1926, **2**, 221), and it has been found that lead tetraethyl and other organometallic compounds which delay detonation in the internal-combustion engine have a marked action in raising the self-ignition temperature.

The action of nitrogen peroxide, *iso*amyl nitrite, and benzoyl peroxide on the self-ignition temperatures of sprays of various substances in air passing through a hot glass tube was studied. The results of a number of experiments are in Table IV, from which it will be seen that nitrogen peroxide is particularly effective, and benzoyl peroxide much less so.

Referring to Table IV(*a*), it was found by an additional experiment that, after the temperature of ignition of the butyl alcohol had been *lowered* to 235° by the addition of 5% (by vol.) of nitrogen peroxide, it could be *raised* to 460° by the addition of 5% (by vol.) of lead tetraethyl. At this temperature the mixture burned with a feeble flame, easily extinguished.

The remarkable lowering of the temperature of inflammation of butyl alcohol from 590° to 235° by the addition of 5% of nitrogen peroxide, and the observed violent explosiveness of the mixture cannot be attributed directly to the liberation of molecular oxygen by the nitrogen peroxide or to its explosiveness, since nitrogen peroxide does not detonate on heating. It is concluded that the effect is due to autoxidation, and that this also accounts for the promotion of detonation in an engine by amyl nitrite and the unstable organic peroxides (Table II).

The theory of autoxidation of fuels in connexion with detonation in the internal-combustion engine has been discussed by Callendar (1927) and the view that peroxidation occurs in the liquid state ha

TABLE IV.

Influence of some peroxides and amyl nitrite on spontaneous ignition temperatures.

(a) Nitrogen peroxide, proportion added, % by vol.	n-Butyl alcohol.	m-Xylene.
0	590°	635°
2·5	355	430
5	235	—

(b) Benzoyl peroxide, proportion added, % by weight.	n-Butyl alcohol.	Ethyl alcohol.	m-Xylene.
0	585°	570°	629°
About 2	560	547	613

(c) *iso*Amyl nitrite, proportion added, % by vol.	n-Butyl alcohol.	m-Xylene.
0	590°	635°
2	552	567
5	545	535
10	518	507
20	455	—

been confirmed by Moureu, Dufraisse, and Chaux (*Compt. rend.*, 1927, **184**, 29), using a different experimental method. It has been demonstrated that the presence of liquid droplets in a gaseous mixture considerably lowers the self-ignition temperature (Bennett and Mardles, J., 1927, 3155; Egerton and Gates, *loc. cit.*).

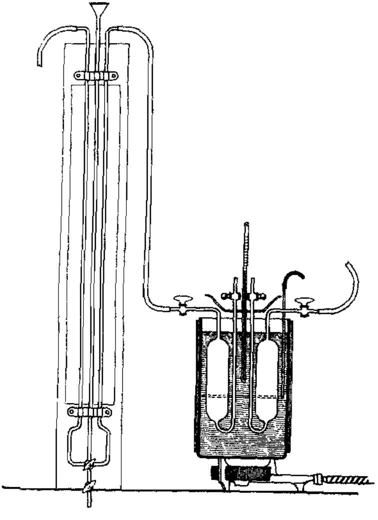
Callendar (1925) showed that lead particles from the thermal decomposition of lead tetraethyl became concentrated on the surface of nuclear drops, which are thus protected against rapid oxidation and early self-ignition, the primary higher oxides formed by the oxygen molecule with the fuel being immediately decomposed by the metal, and autoxidation being thus delayed.

Egerton and Gates, in order to determine the effect of the metal constituent of dopes, carried out experiments with metal vapours from low-tension arcs, and found that lead vapour behaved similarly to lead tetraethyl in raising the ignition temperature of petrol and in delaying detonation in the internal-combustion engine, a result which is strong evidence for the conclusion that the efficacy of lead tetraethyl is due to the metallic lead formed by thermal decomposition. A similar conclusion has been reached by other investigators from other points of view (*e.g.*, Church, Mack, and Boord, *Ind. Eng. Chem.*, 1926, **8**, 334; Sims and Mardles, *Trans. Faraday Soc.*, 1926, **22**, 363).

Egerton and Gates have advanced the view that aldehydes, which they regard as having been produced in accord with the well-known hydroxylation theory of combustion of hydrocarbons, form peroxides, which autocatalyse the combustion, giving rise to detonation. This view cannot be maintained in the light of engine

experiments which show that aldehydes do not increase but rather delay detonation. This result was one of the principal reasons for the replacement of the hydroxylation theory by the autoxidation theory of combustion, the hydroxyl compound which preceded the aldehyde formation, according to the hydroxylation theory, being also a substance not liable to detonate.

FIG. 2.

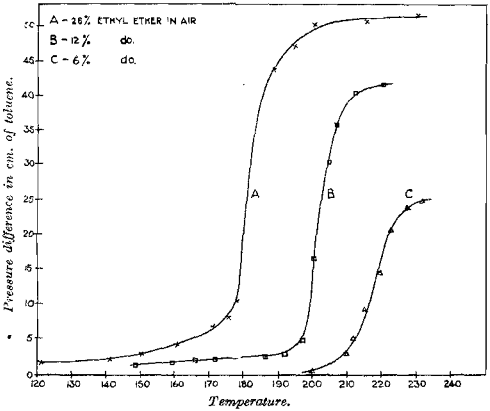


(b) Initial Combustion of Hydrocarbon–Air Mixtures. Bulb Metho

The bulb method has already been described briefly. Th arrangement of the apparatus is shown by Fig. 2. Two simila bulbs, which can be heated equally in a well-stirred oil-bath, a connected differentially to a toluene manometer, as in Callendar compensated gas-thermometer; one is filled with dry air and th other with the hydrocarbon–air mixture under test. The increa of pressure due to heating is balanced by the differential arrang ment, and the toluene manometer measures the pressure increa

due to combustion only. This differential method is about 100 times more sensitive than the single-bulb method in general use, in which a *mercury* manometer is used to measure the *sum* of the increases of pressure due to (1) heating and (2) the augmented number of molecules in the mixture due to the chemical reaction. *An essential feature of the new design is the provision of tubes and taps at both ends of the bulbs, which greatly facilitate cleaning and drying, and make it easy to fill either bulb at any time with definite mixtures of known strength.*

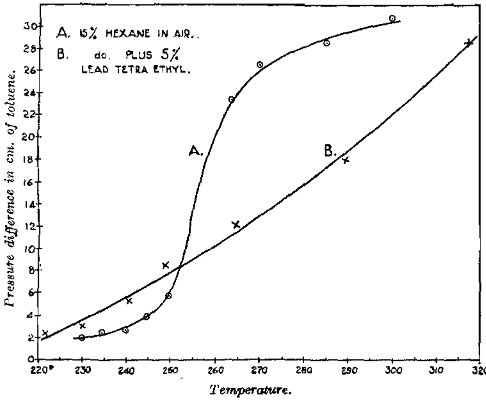
FIG. 3.



Description of Curves obtained by Bulb Method.—In the interpretation of these curves it must be borne in mind that, whereas in the tube method a continuous flow of mixture is exposed to a very rapid rise of temperature for a short time rarely exceeding 1 minute, in the bulb method a constant volume of mixture is continuously exposed to a slow rise of temperature until the reaction is complete. A few typical curves illustrating the results thus obtained are shown in Figs. 3, 4, and 5. Those in Fig. 3 illustrate the case of simple ether-air mixtures of different strengths, and completely confirm the results of the tube method. The curves are of the usual sigmoid type, and show that the reaction starts very slowly at first,

but that the rate increases exponentially with rise of temperature, becoming very rapid at a fairly definite temperature, and slowing down again as the reaction approaches completion. When the mixture strength is *reduced*, the curve is shifted in the direction of higher temperature by nearly 20° each time the strength is halved, as shown by the curves B and C. This indicates that the reaction is not merely a question of temperature, and that the starting point cannot be stated definitely within 1° or 2° (Lewis, J., 1927, 1560). It further supports the conclusion drawn from the tube method, that the reaction is due primarily to the formation of some very

Fig. 4.



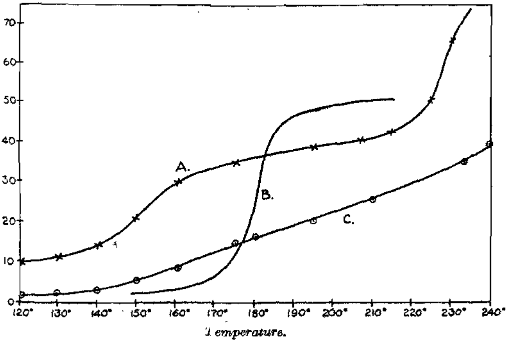
active and short-lived additive compound, probably a peroxide, indications of which were found in the products. Since it has been shown that a reaction of this type occurs most readily in the liquid phase, the effect of mixture strength in lowering the temperature of initial combustion is immediately explained on the nuclear theory by the observation that nuclear drops are formed more readily in strong mixtures than in weak.

The curves shown in Fig. 4 illustrate the effect of adding 5% of lead tetraethyl to a 15% hexane–air mixture. The hexane–air mixture by itself gives a curve A very similar to those in Fig. 3, except that the reaction starts at a higher temperature and is less

rapidly completed than in the case of ether. The effect of a 5% addition of lead tetraethyl is shown by curve B, which appears simpler at first sight but is in reality more complex owing to the presence of three primary components of the reaction; this curve has been corrected (by a separate experiment) for the effect of the decomposition of the lead tetraethyl when mixed with air in the absence of hexane. It has already been shown by the tube method that the first effect of this addition to a hexane–air mixture is to lower the temperature at which the reaction starts, owing to action at the surface of the liberated metal. This effect is confirmed by

FIG. 5.

A *Ether–air mixture plus 5% lead tetraethyl.*
B *Ether–air mixture alone.*
C *Curve "A" corrected for pressure rise due to oxidation of lead tetraethyl alone.*



the bulb method. The subsequent course of the reaction is completely modified by the suppression of active oxygen (as demonstrated by the tube experiments) which wipes out the steep rise of the hexane curve A, attributed to autoxidation, by preventing the accumulation of peroxides in sufficient quantity to autocatalyse the reaction.

It is clear that the formation of short-lived peroxides could not be expected to cause any appreciable drop of pressure in the initial stages of the reaction, because any such effect would be more than compensated by their rapid decomposition.

The curves in Fig. 5 (in which the pressure scale is half that of

Figs. 3 and 4) show the effect of lead tetraethyl on a rich ether–air mixture similar to A in Fig. 3. It has already been shown (Callendar and others, R. & M. 1013; *Engineering*, April 9th, 1926, *et seq.*) that the presence of ether induces oxidation and decomposition of the lead compound at much lower temperatures than the presence of hexane. This is confirmed by the first part of curve A in Fig. 5, where the increase of pressure shown is due almost entirely to this cause. The corrected curve C, in which this effect is allowed for, is very similar to that found in the case of hexane. Sufficient lead remains, presumably in the nuclei where it would naturally be concentrated, to obliterate the autoxidation stage of the ether curve B at the normal temperature of 180°. But a much larger proportion of lead tetraethyl is required to produce this effect in the bulb method than to prevent detonation in an engine, since it is not merely a question of delaying the reaction for a small fraction of a second as in the engine, but of providing sufficient lead to prevent oxidation of the fuel in the bulb at a given temperature when unlimited time is allowed.

Results and Conclusions.

(*a*) The yield of active oxygen obtained during the slow oxidation of fuel–air mixtures is greatly diminished if heating of the mixture is continued longer than is required for the initial formation of the peroxide, showing that the primary peroxides, owing to their great activity, are very short-lived.

(*b*) The activity of the primary peroxides formed in hexane–air or ether–air mixtures is also demonstrated by the autoxidation of benzene and aniline, which occurs readily in the presence of hexane or ether but cannot be induced at equally low temperatures in their absence.

(*c*) The effects mentioned have been attributed by others to the action of hydrogen peroxide, but the experiments now described lead to the conclusion that the hydrogen peroxide produced from combustion in the heated tube or in the engine during compression is a decomposition product arising from much more active and unstable peroxides previously formed.

(*d*) The experimental work confirms the view (R. & M. 1062) that detonation in an engine using liquid fuel is due to the formation of organic peroxides, which become concentrated in the nuclear drops during compression and ignite them simultaneously when the detonation temperature of the peroxide is reached. The addition of detonation-inducers (such as nitrogen peroxide, amyl nitrite, and benzoyl peroxide) to a variety of fuels shows that the temperature of spontaneous ignition is lowered in all cases, and

detonation-preventers (such as certain organo-metallic compounds) have the opposite effect.

Acknowledgment is made to Professor H. L. Callendar, F.R.S., for his inspiring help, especially with regard to suitable methods and interpretation of the experimental results.

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AIR MINISTRY LABORATORY, IMPERIAL COLLEGE OF SCIENCE,
LONDON, S.W. 7. [*Received, January 2nd*, 1928.]

CXVIII.—*The Absorption Spectra of Anthracene Derivatives. Part I.*

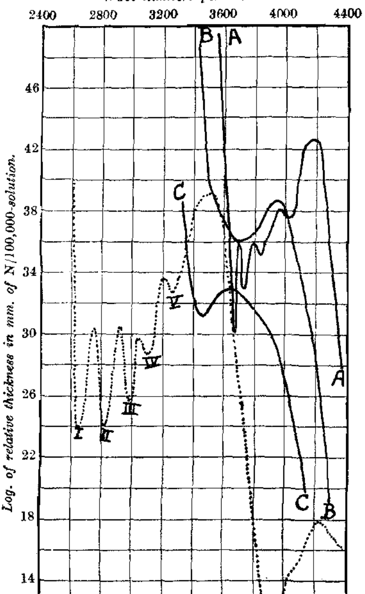
By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and THOMAS ERIC ELLISON.

THE study of the valency problem presented by the *meso*-carbon atoms of anthracene has led to the discovery of many apparently anomalous reactions, the interpretation of which by purely chemical methods is difficult. It is proposed, therefore, to consider the evidence afforded by spectrophotography; and in the first place the effect produced on the spectrum by certain modifications of the molecule will be discussed.

Anthracene itself has been examined by numerous investigators. The absorption spectrum of the alcoholic solution, as obtained by the Hartley method, shows six bands (Fig. 1), each subdivisible by more refined methods into two or more components (Capper and Marsh, J., 1926, 724); for ease of reference these are numbered I to VI in the figure and in the table. There is an approximately constant frequency difference between each of the bands I to V. As long as the so-called " bridge " bond is present, the introduction of other groups into the *meso*-positions of anthracene has remarkably little effect on the spectrum. The mass of the substituent has an almost negligible influence on the amount of the displacement, one alkyl, alkyloxy, phenyl or benzyl group moving the spectrum as a whole 60—80 units of frequency towards the visible region, the position of band VI always being altered less than the positions of bands I to V. Thus the band heads of 9-methyl- and 9-benzylanthracene are at the same frequencies. In these *meso*-substituted derivatives band II is slightly more persistent than band I, the reverse being the rule elsewhere. The introduction of a second substituent causes a further shift of about 70 units towards the visible region, corresponding bands of anthracene and 9-methyl-

10-phenylanthracene, for example, having a *frequency difference* of about 140 units. In these 9 : 10-disubstituted anthracenes band V ceases to be detectable.

FIG. 1.



····· *Anthracene.* B 1 : 5-*Dichloro*-9 : 10-*dihydroanthraquinol.*
A 9 : 10-*Dihydroanthracene.* C 1 : 5 : 9 : 10-*Tetrachloro*-9 : 10-*dihydroanthracene.*

1 : 5-Dichloroanthracene and a few of its mono- and di-substitution products have also been examined. The effect of the chlorine atoms is to move the whole spectrum towards the visible region, bands I to V being moved 90—95 units and band VI about

30 units in accordance with the above-mentioned rule that the position of band VI is invariably less affected by substitution than are the other five. No other alteration of the spectrum is observed, despite the profound influence of α-chlorine atoms on the chemical behaviour of the *meso*-carbon atoms. The effects of further substitution on the spectrum of 1 : 5-dichloroanthracene are similar to those found with anthracene itself.

9 : 10-Dihydroanthracene has been examined by Baly and Tuck (J., 1908, **93**, 1902), but the evident impurity of their specimen has made a re-examination desirable, and it has now been found that the spectrum resembles that of an alkyl derivative of benzene, four major band heads being detectable at 3660, 3730, 3830, and 4020 (Fig. 1). The effect of reduction on the fluorescence and absorption of anthracene is therefore analogous to that found in the acridine series (Dobbie and Tinkler, J., 1905, **87**, 269). In the allied substances 1 : 5 : 9 : 10-tetrachloro-9 : 10-dihydroanthracene and 1 : 5-dichloro-9 : 10-dihydroanthraquinol, the complex band system of the more symmetrical dihydroanthracene is fused into a single broad band, which on account of the mass of the substituents is nearer to the visible region than are the bands of dihydroanthracene itself. Evidently the curve of this class of derivative has no detail in common with that of anthracene.

The anthrones present a third type of derivative and a few of these have been examined. Anthrone itself, being in tautomeric equilibrium with anthranol, may be expected to possess a complex spectrum, but where, by replacement of the methylene hydrogen atoms by non-mobile groups, the possibility of such tautomeric change is excluded, a characteristic curve containing one broad, indefinite and shallow band is obtained. The spectra of 9 : 9-dimethyl-, 9 : 9-diphenyl-, and 9 : 9-dibenzyl-anthrone are shown in Fig. 2.

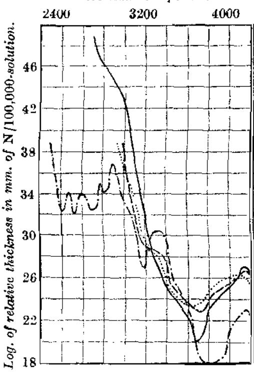
The Mechanism of Bromination of meso-*Alkylanthracenes*.—The facile formation of ω-bromo-derivatives of 9-alkyl- and 9 : 10-dialkyl-anthracenes has been discussed elsewhere (Barnett, Cook, and Matthews, *Ber.*, 1926, **59**, 1429, 2863; 1927, **60**, 2353, 2366), and an explanation suggested based on the possible transannular tautomerism according to the scheme :

$$C_6H_4 < \underset{CH}{\overset{C\cdot CH_3}{|}} > C_6H_4 \rightleftharpoons C_6H_4 < \underset{CH_2}{\overset{C:CH_2}{}} > C_6H_4$$

The presence of the methylene phase would readily account for the side-chain bromination by addition of bromine to the double bond and elimination of hydrogen bromide across the ring. More definite

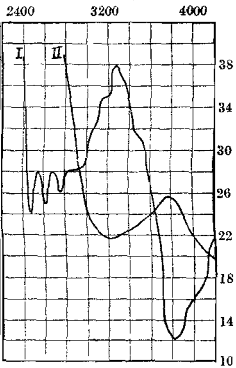
evidence of this type of tautomerism has been sought in a study of the spectra of the *meso*-alkylanthracenes, since a tautomeric change of this type might be indicated spectroscopically in two ways, *viz.*, the curve might show bands characteristic of both the extreme phases of the oscillation, and it might show modifications due to the actual oscillation itself. The point may be illustrated by

FIG. 2.



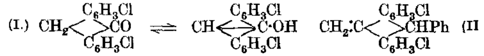
——— 9 : 9-*Dimethylanthrone.*
· · · · · 9 : 9-*Diphenylanthrone.*
— — — 9 : 9-*Dibenzylanthrone.*
—·—·— 1 : 5-*Dichloroanthrone.*

FIG. 3.



I *Yellow derivatives of* 1 : 5-*dichloro-benzylanthracene* (*formula V*).
II *Colourless derivatives of* 1 : 5-*dichlo*
9-*benzylanthracene* (*formula III or I*

reference to 1 : 5-dichloroanthrone (I), the curve of which is show in Fig. 2.

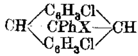


In this the anthracene bands are well marked, although less p sistent than usual. The band with head at 3850 is of distinct anthrone type, whereas the band with head at 3190 is possibly d to the tautomeric change.

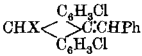
The spectra of the alkylanthracenes which possess the prope of easy side-chain bromination have been examined along w those of certain other *meso*-substituted anthracenes such as 9-me

oxy- and 9-acetoxy-anthracene for the purposes of comparison, but a deviation from the normal the occurrence of which would support the hypothesis of transannular tautomerism has not been detected. The spectra have also been examined in the presence both of hydrochloric acid and of sodium ethoxide, but neither acid nor alkali produces any observable effect. The very nature of the method, however, makes it impossible to say that tautomerism does not occur, particularly as selective absorption can scarcely be detected in 1 : 5-dichloro-10-phenyl-9-methylene-9 : 10-dihydroanthracene (II), the only compound known definitely to have the methylene structure which has been examined up to the present.

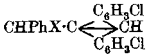
Derivatives of 1 : 5-*Dichloro-9-benzylanthracene.*—It has been shown (Barnett, Cook, and Matthews, *loc. cit.*) that 1 : 5-dichloro-9-benzylanthracene yields two series of isomeric derivatives, *viz.*, a colourless series obtained by direct replacement of the bromine atom in the bromo-compound (of which only one isomeride is known) and a yellow series obtained from the colourless compounds by isomeric change. An examination of the absorption spectra of the bromo-compound and of the colourless hydroxy- and methoxy-compounds (curve II, Fig. 3) has shown that the curves are indistinguishable from one another in the region examined (solutions of the bromo-compound could not be examined in higher concentration than $M/10,000$ on account of its instability and slight solubility). This is in agreement with the view already expressed, that the bromo-compound has a structure corresponding to that of the colourless series. The absorption curve, however, does not lead to a decision between the alternative structures (III and IV) suggested for these colourless compounds, as reference compounds of the two types are not available at present :



(III.)



(IV.)



(V.)

The yellow hydroxy- and methoxy-compounds, on the other hand, give curves (curve I, Fig. 3) of the true " anthracene " type which are indistinguishable from that of 1 : 5-dichloro-9-benzylanthracene, and this is in harmony with the chemical evidence of the formula (V) already given to these compounds.

The indiscriminate manner in which special structures, especially quinonoid, are assigned to organic compounds for no other reason than the possession of visible colour makes it of interest to note that in all the " bridge " compounds dealt with in this communication the electronic structure of the anthracene complex remains

the same although the visible colour ranges from colourless in the case of anthracene to greenish-yellow in the case of some of the derivatives of 1 : 5-dichloroanthracene.

The greatest care has been taken to obtain all the substances used as pure as possible, every sample having been repeatedly recrystallised after the melting point had become constant. All the spectra were taken in ethyl-alcoholic solution.

Table of Bands.

Substituents.				Oscillation frequencies.					
1	5	9	10	I.	II.	III.	IV.	V.	VI.
				2660	2810	2970	3100	3250	3930
		COPh		2610	2750	2890	—	3180	3910
		OAc		2600	2740	2890	3020	3170	3890
		Ph		2600	2730	2880	3000	3170	3860
		OMe		2580	2730	2870	3000	3160	3860
		Me		2580	2720	2850	2990	3160	3850
		CH_2Ph		2580	2720	2850	2990	3160	3850
		Pr^{β}		2580	2730	2870	2990	3140	3850
		iso-C_5H_{11}		2570	2720	2850	2990	3140	3850
Cl	Cl			2570	2720	2850	2990	3140	3900
		Me	Ph	2520	2670	2820	2980	—	3840
		Ph	Ph	2520	2670	2820	2980	—	3840
		iso-C_5H_{11}	Ph	2520	2660	2820	2970	—	3840
Cl	Cl	OAc		2510	2650	2790	2970	—	3890
Cl	Cl	Me		2490	2630	2760	—	—	3850
Cl	Cl	CH_2Ph		2490	2620	2760	—	—	3830
Cl	Cl	CH(OH)Ph		2490	2620	2760	—	—	3830
Cl	Cl	CH(OMe)Ph		2490	2620	2760	—	—	3830
Cl	Cl	CH_2Br		2430	2550	—	—	—	3790
Cl	Cl	Ph	CH_2Ph	2420	2530	2680	2830	?	3760
Cl	Cl	Anthrone *		2420	2530	2680	2820	—	—

* 1 : 5-Dichloroanthrone also has bands at 3190 and 3850.

The authors' thanks are due to Professor A. W. Stewart for the interest he has taken in this work.

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JEWRY STREET, E.C. 3. [*Received, January 14th, 1928.*]

CXIX.—*The Complex Salts of Bivalent Platinum with αβγ-Triaminopropane.*

By FREDERICK GEORGE MANN.

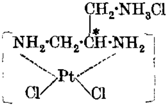
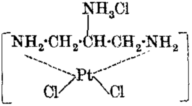
IT has already been shown by the present author (J., 1926, 2681; 1927, 1224) that chloroplatinic acid co-ordinates with triaminopropane trihydrochloride to give tetrachloro(triaminopropane-γ-monohydrochloride)platinum,

$$[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HCl],H_2O,$$

a compound whose resolution into optically active forms proves that the platinum is co-ordinated only to the α- and β-amino-groups, leaving the γ-amino-group free to form a hydrochloride. It is now found that if potassium chloroplatinite is treated with triaminopropane trihydrochloride, *dichloro(triaminopropane-monohydrochloride)platinum monohydrate*,

$$[Cl_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HCl],H_2O,$$

is formed similarly. This compound, like the tetrachloro-compound, might exist in two forms, one in which co-ordination occurs through the α- and β-amino-groups, giving a γ-monohydrochloride (I),

(I.)   (II.)

and the other in which co-ordination occurs through the α- and *γ-amino-groups, giving a* β-monohydrochloride (II). These isomerides differ fundamentally in that (I) is dissymmetric, having the β-carbon atom (marked *) asymmetric, whereas (II) is symmetric. The resolution of this compound into optically active forms, described in the present paper, proves it to have the former constitution, being, like the tetrachloro-compound, a γ-monohydrochloride. It is therefore the second known compound in which asymmetry of a *carbon atom is induced by the operation* of auxiliary valencies.

The properties of dichloro(triaminopropane-γ-monohydrochloride)-platinum resemble closely those of the tetrachloro-compound; *e.g.*, the two optically active forms are both anhydrous, and the racemic product is a monohydrate. The most characteristic salt is again the *γ-monohydrogen oxalate*,

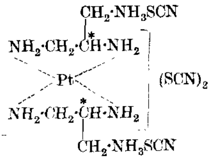
$$[Cl_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,(CO_2H)_2],$$

which is rapidly precipitated when the monohydrochloride is treated in solution with oxalic acid. Furthermore, if the monohydrochloride is treated with ammonia, the latter withdraws the hydrogen chloride, and the amino-group liberated immediately co-ordinates with the platinum, expelling a chlorine atom from the complex and giving *monochlorotriaminopropaneplatinous monochloride*,

$$[ClPtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2]Cl.$$

Treatment of potassium chloroplatinite with an excess of triaminopropane base instead of the trihydrochloride gives rise, however, to two entirely different types of complex salt. Co-ordination in these circumstances is rapid, giving a colourless solution: if this is now concentrated, acidified with acetic acid, and treated with potassium thiocyanate, the white crystalline *bis(tri-*

aminopropane-monothiocyanate)platinous dithiocyanate (III) is produced. In this compound each molecule of the base is co-ordinated

(III.) 

to the metal by only two of its three amino-groups, leaving the third free for normal salt formation as a thiocyanate : the 4-co-ordination platinous atom, being thus saturated, also forms a dithiocyanate, and the compound in solution furnishes, in all, four thiocyanate ions. This compound is therefore of precisely the same type as the cupric compound already described (*loc. cit.*). The work of Mills and Gotts (J., 1926, 3121) has shown that in such cupric compounds the four co-ordination valencies are directed to the apices of a tetrahedron, and the very close resemblance in type and properties between these cupric and platinous compounds would show that the latter also probably have the tetrahedral configuration. Experimental evidence for this is unfortunately difficult to obtain. It will be seen that the platinous compound (III) has two asymmetric carbon atoms, and should therefore exist in racemic and *meso*-forms by virtue of these carbon atoms alone : in both forms, however, the complex itself, if tetrahedrally arranged, is dissymmetric and should be capable of further resolution into optically active forms. Mere resolution of the compound, therefore, gives no evidence as to the configuration of the platinous complex itself. Such evidence could only be obtained by separating the racemic and the *meso*-forms, and then resolving the latter form : this " secondary " activity could not be due to the asymmetric carbon atoms, and would thus prove the tetrahedral configuration of the platinous complex. Actually the platinous thiocyanate, like the cupric compound, is a crystalline compound of sharp melting point, and is obviously a single chemical individual : no evidence of the existence of two forms, racemic and *meso*, could be obtained.

If now the colourless solution obtained by treating potassium chloroplatinite with the free base is concentrated and then, without the addition of acid, is treated with potassium iodide solution, *bis(triaminopropane)platinous di-iodide*,

$$[Pt\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_2]I_2,$$

is precipitated. This would appear to be a novel type of compound

in which the bivalent platinum atom has a co-ordination number of 6 instead of its usual number of 4. There remains a second possibility, *viz.*, that this compound is of precisely the same type as the thiocyanate (III), but that, in the absence of acid, the two γ-amino-groups exist free, being neither co-ordinated to the metal nor neutralised by acid. This is, however, unlikely, since on crystallisation from aqueous solution each free amino-group would almost undoubtedly add on a molecule of water to give a substituted ammonium hydroxide, as in the cupric ethylenediaminobisacetylacetone ethylenediamine hydrate described by Morgan and Smith (J., 1926, 918). The existence of two free γ-amino-groups was, however, completely disproved by treating the di-iodide in aqueous solution with an excess of free picric acid : a *dipicrate* alone was obtained, showing that all six amino-groups are co-ordinated to the platinum atom. Had the two γ-amino-groups been free, the di-iodide should have given a tetrapicrate, since, in addition to the dipicrate of the complex, each free amino-group would also unite with picric acid.

These are the first compounds to be described in which a bivalent platinum atom has a co-ordination number of 6. They serve to illustrate one respect in which the stability of the complex salts with simple molecules, *e.g.*, ammonia and water, differs from that of complex salts with polyamine molecules, *e.g.*, triaminopropane. The stability of the simple ammines is determined primarily by the electronic structure of the metal when thus co-ordinated, *e.g.*, cobalt of atomic number 27 requires 9 electrons to complete its outer shell and in $[(NH_3)_6Co]Cl_3$ these 9 are obtained (+ 12 − 3) and an extremely stable salt results. Platinum of atomic number 78 requires 8 electrons to complete its outer shell. In the platinic series, *e.g.*, $[(NH_3)_6Pt]Cl_4$, these are again acquired, giving a very stable salt, whereas in the platinous series, *e.g.*, $[(NH_3)_4Pt]Cl_2$, only 6 are obtained ; since, however, a small deficiency of electrons is more readily tolerated than an excess, these tetramminoplatinous salts are stable, although less so than the hexamminoplatinic salts. The stability of the complex salts of the polyamines is dependent, however, on an additional factor, *viz.*, the comparative ease with which the polyamine molecule, for purely structural reasons, can arrange itself about a complex that may be a square, a tetrahedron, or an octahedron. There is considerable evidence to show that triaminopropane adjusts itself readily and very stably to the 6-co-ordination octahedron (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **107**, 80 ; J., 1926, 2675). The great stability of the bis(triaminopropane)-cobaltic and -rhodium trihalides is to be expected, since the metallic atoms here have completed their electronic outer shells

in the usual way. But in the case of nickel, the tetramminonickelous dihalides, *e.g.*, $[(NH_3)_4Ni]Cl_2$, in which the metal has a deficiency of 2 electrons, are far more stable than the hexamminonickelous dihalides, *e.g.*, $[(NH_3)_6Ni]Cl_2$, in which the metal has a *surplus of 2 electrons*. Yet nickel combines with triaminopropane to give always the very stable bis(triaminopropane)nickelous salts, *e.g.*, $[\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_2Ni]I_2$, in which the metal has a co-ordination number of 6, and no triaminopropane salt in which the nickel has a co-ordination number of 4 has yet been isolated. Triaminopropane thus adjusts itself so much more stably around the 6-co-ordination octahedron than around a tetrahedron or a square that a metallic atom, normally of co-ordination number 4, will sometimes increase the latter to 6 in order to accommodate itself to the triamine, although for purely electronic reasons such an arrangement would be regarded as unstable. A further example of this is provided by the bis(triaminopropane)platinous dihalides now described, in which the bivalent platinum has increased its co-ordination number to 6 in order to provide the octahedron necessary for stable co-ordination with triaminopropane, although the metallic atom has thereby acquired an excess of 2 electrons.

When triaminopropane co-ordinates by means of only two of its three amino-groups, the above considerations no longer hold, and stable 4-co-ordination derivatives, *e.g.*, of platinum and copper, result.

Ammonium chloropalladite co-ordinates with triaminopropane trihydrochloride to give *dichloro(triaminopropane-monohydrochloride)palladium*, $[Cl_2PdNH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2,HCl]$. This salt proved to be unstable in hot aqueous solution, and therefore no attempts were made to resolve it into optically active forms.

EXPERIMENTAL.

All rotations given in this paper have been measured at 15° in a 4-dm. polarimeter tube by means of the mercury green line ($\lambda =$ 5461).

Dichloro(triaminopropane-γ-monohydrochloride)platinum Monohydrate.—Potassium chloroplatinite (16 g.) and triaminopropane trihydrochloride (16 g.) were dissolved in turn in water (240 c.c.), and the solution was boiled under reflux for 2 hours, the deep red colour changing to orange. The solution was concentrated until crystals appeared, then filtered and chilled. The crude product (11·8 g.), when recrystallised from hot water, gave the above *monohydrate* in pale yellow crystals, which darken at 280° and melt at 290—291° (decomp.) (Found: C, 8·9; H, 3·4; N, 9·9; Pt, 47·6; H_2O, 4·4. $C_3H_{12}N_3Cl_3Pt,H_2O$ requires C, 8·8; H, 3·4; N, 10·25; Pt, 47·6; H_2O, 4·4%).

d-*Dichloro(triaminopropane-mono*-d-*bromocamphor-π-sulphonate)-platinum Monohydrate*,

$[Cl_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,C_{10}H_{14}OBr{\cdot}SO_3H],H_2O$.
—Hot aqueous solutions of dichloro(triaminopropane-monohydrochloride)platinum monohydrate (12 g.) and silver *d*-bromocamphor-sulphonate (13·2 g.) were mixed, boiled for 5 minutes, and filtered. The filtrate, when concentrated and cooled, deposited orange-yellow crystals, which, after five recrystallisations from water, gave the above optically pure d-*base* d-*sulphonate* (Found: C, 22·8; H, 4·2; Pt, 28·4. $C_{13}H_{28}O_5N_3Cl_2BrSPt$ requires C, 22·8; H, 4·1; Pt, 28·5%). A 0·5773% aqueous solution had $\alpha = +1{\cdot}76°$, whence $[\alpha] = +76{\cdot}2°$, $[M] = +522°$.

d-*Dichloro(triaminopropane-monohydrochloride)platinum*.—A solution of the above optically pure *d*-base *d*-sulphonate in the minimum of hot water was diluted with a hot concentrated solution of calcium chloride, filtered, and chilled. After 24 hours, the anhydrous crystalline d-*monohydrochloride* which had separated was filtered off, washed with alcohol and ether, and dried (Found: Pt, 50·0. $C_3H_{12}N_3Cl_3Pt$ requires Pt, 49·8%). A 1·051% aqueous solution had $\alpha = +2{\cdot}09°$, whence $[\alpha] = +49{\cdot}7°$, $[M] = +195°$.

l-*Dichloro(triaminopropane-mono*-l-*bromocamphor-π-sulphonate)-platinum Monohydrate*.—This separated from a saturated aqueous solution of the racemic monohydrochloride when the latter was diluted with a concentrated solution of ammonium *l*-bromocamphor-sulphonate, and again five recrystallisations from water furnished the optically pure l-*base* l-*sulphonate* (Found: Pt, 28·65%). A 0·5032% aqueous solution had $\alpha = -1{\cdot}54°$, whence $[\alpha] = -76{\cdot}5°$, $[M] = -524°$.

l-*Dichloro(triaminopropane-monohydrochloride)platinum* was prepared as pale yellow crystals by treating the *l*-base *l*-sulphonate in solution with calcium chloride (Found: Pt, 49·9%). A 1·279% aqueous solution had $\alpha = -2{\cdot}51°$, whence $[\alpha] = -49{\cdot}1°$, $[M] = -192°$.

Dichloro(triaminopropane-mono-d-*camphor-β-sulphonate)platinum*, $[Cl_2PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,C_{10}H_{15}O{\cdot}SO_3H]$, was isolated in a similar way to the bromocamphorsulphonate by the interaction of the monohydrochloride (10 g.) and silver *d*-camphorsulphonate (8·4 g.). Two recrystallisations from water gave the d-*camphor-sulphonate* as a pale yellow, crystalline powder (Found: C, 26·5; H, 4·7; Pt, 33·1. $C_{13}H_{27}O_4N_3Cl_2SPt$ requires C, 26·6; H, 4·6; Pt, 33·2%). A 1·294% aqueous solution had $\alpha = +0{\cdot}54°$, whence $[\alpha] = +10°$, $[M] = +61°$. The material was now recrystallised three times, and then in a 1·463% solution had $\alpha = +0{\cdot}58°$, whence $[\alpha] = 9{\cdot}9°$, $[M] = +58°$. As the average rotation found by

Graham (J., 1912, **101**, 746) for the camphor-β-sulphonate ion is 65·8°, it was obvious that the resolution was proceeding very slowly, and no further experiments were made with this salt.

Dichloro(triaminopropane - hydrogen - oxalate)platinum. — When aqueous solutions of the monohydrochloride and of oxalic acid were mixed, the above *hydrogen oxalate* rapidly separated as an orange crystalline powder, only slightly soluble in cold water. It was recrystallised from hot water and then, since the water of crystallisation was only slowly lost in a desiccator, it was dehydrated by heating at 95° in a vacuum. The anhydrous material had m. p. 216—217° (decomp.) with preliminary darkening (Found : C, 13·2; H, 3·1; Pt, 44·2. $C_5H_{13}O_4N_3Cl_2Pt$ requires C, 13·5; H, 2·9; Pt, 43·8%).

Monochlorotriaminopropaneplatinous Monochloride. — When aqueous ammonia was added to a concentrated aqueous solution of the monohydrochloride, a yellow crystalline precipitate rapidly separated. This was insoluble in cold water, and dissolved in hot water only with decomposition, since such solutions slowly deposited a white product. It was therefore filtered off, washed with cold water, and dried, and the above *monochloride* was thus obtained in yellow crystals, m. p. 282—283° (decomp.) (Found : C, 10·0; H, 3·15; Pt, 54·8. $C_3H_{11}N_3Cl_2Pt$ requires C, 10·1; H, 3·1; Pt, 54·95%).

Bis(triaminopropane-monothiocyanate)platinous Dithiocyanate (III).—Triaminopropane trihydrochloride (9·4 g.), dissolved in water (50 c.c.), was treated with 15% sodium hydroxide solution (34·8 c.c.), and this solution of the free base was now added to potassium chloroplatinite (6 g.), also dissolved in water (50 c.c.). When the final solution was heated on a water-bath, the red colour faded and a buff-coloured precipitate separated: this slowly redissolved, and the now colourless solution was concentrated, chilled, filtered from any sodium chloride, acidified with acetic acid, and treated with concentrated potassium thiocyanate solution, also containing acetic acid. The white precipitate which slowly separated was filtered off after 24 hours, and twice recrystallised from hot water, in which it was very soluble. The above *dithiocyanate* was obtained in white crystals, m. p. 177—178° (Found : C, 19·7; H, 4·0; Pt, 32·15; ionised SCN, 38·2. $C_{10}H_{24}N_{10}S_4Pt$ requires C, 19·7; H, 4·0; Pt, 32·1; 4SCN, 38·2%).

Bis(triaminopropane - mono - d - bromocamphorsulphonate)platinous Di-d-bromocamphorsulphonate Trihydrate,

$[Pt\{NH_2·CH_2·CH(NH_2)·CH_2·NH_2,C_{10}H_{14}OBr·SO_3H\}_2](C_{10}H_{14}OBr·SO_3)_2,3H_2O$.

—Hot aqueous solutions of the thiocyanate (4 g.) and silver *d*-bromo-

camphorsulphonate (11·7 g.; 4 mols.) were mixed. Concentration of the filtered solution gave the white crystalline *bromocamphorsulphonate trihydrate*, which was recrystallised seven times from water (Found: C, 32·9; H, 5·3; Pt, 11·7. $C_{46}H_{80}O_{16}N_6Br_4S_4Pt,3H_2O$ requires C, 33·0; H, 5·2; Pt, 11·7%). A 0·5184% aqueous solution had $\alpha = +1·66°$, whence $[\alpha] = +80·1°$, $[M] = +1340°$. Since the bromocamphorsulphonate ion has $[M] = 347°$ (Pope and Read, J., 1910, **97**, 2201), the rotation was due to the four sulphonate ions alone.

Bis(triaminopropane)platinous Di-iodide.—The preparation was carried out precisely as for the above thiocyanate, but the final concentrated colourless solution was treated directly with saturated potassium iodide solution, without addition of acetic acid. The fine, white precipitate was twice recrystallised from a little hot water, and the above *di-iodide* obtained as fine white crystals, m. p. 266—267° (decomp.) (Found: C, 11·8; H, 3·5; I, 40·9; Pt, 31·2. $C_6H_{22}N_6I_2Pt$ requires C, 11·6; H, 3·6; I, 40·5; Pt, 31·1%).

The corresponding *dibromide* was similarly obtained by treating the final colourless solution with saturated sodium bromide solution. After recrystallisation from water, it was obtained in white crystals, m. p. 270—271° (decomp.), far more soluble than the iodide (Found: C, 13·6; H, 4·2; Pt, 36·6. $C_6H_{22}N_6Br_2Pt$ requires C, 13·5; H, 4·2; Pt, 36·6%).

Bis(triaminopropane)platinous Dipicrate,

$$[Pt\{NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot NH_2\}_2](C_6H_2(NO_2)_3\cdot O)_2.$$

—A dilute solution of the above dibromide was added to a considerable excess of aqueous picric acid solution; the yellow precipitate produced was collected after 2 hours, washed with much cold water, in which it was almost insoluble, and dried. The *dipicrate* was thus obtained as a fine, yellow powder, which deflagrated violently when heated (Found: N, 20·1; Pt, 23·7. $C_{18}H_{26}O_{14}N_{12}Pt$ requires N, 20·3; Pt, 23·5%).

Dichloro(triaminopropane-γ-monohydrochloride)palladium.—Ammonium chloropalladite (3 g.) and triaminopropane trihydrochloride (6·9 g.; 3 mols.) were in turn dissolved in water (50 c.c.) and the clear solution was boiled under reflux for 4 hours, the colour fading to a pale golden-brown. The solution was filtered and allowed to cool in a closed vessel; fine, yellowish-brown crystals were deposited over-night. These were recrystallised as rapidly as possible from a little hot water, and the above *monohydrochloride* obtained in minute, golden-brown crystals, m. p. 279—280° (decomp.) (Found: C, 11·9; H, 4·0; N, 14·1; Pd, 35·3. $C_3H_{12}N_3Cl_3Pd$ requires C, 11·9; H, 4·0; N, 13·9; Pd, 35·2%).

Triaminopropane Trihydrogen Trioxalate Monohydrate, $C_3H_5(NH_2,HO_2C{\cdot}CO_2H)_3,H_2O$.—When aqueous solutions of the trihydrochloride and of oxalic acid are mixed, the very characteristic *trihydrogen trioxalate* rapidly separates in white needles, m. p. 173—174° (decomp.) after recrystallisation from hot water. The oxalate is only slightly soluble in cold water, but is freely soluble in hot water (Found: C, 28·8; H, 5·1. $C_9H_{17}O_{12}N_3,H_2O$ requires C, 28·6; H, 5·1%).

The author is greatly indebted to Professor Sir William Pope, F.R.S., for the supplies of platinum and of *l*-camphor used in this investigation.

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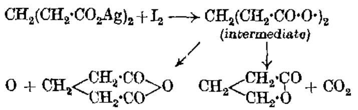
CXX.—*The Influence of Groups and Associated Rings on the Stability of Certain Heterocyclic Systems. Part IV. The Substituted Butyro- and Valero-lactones.*

By SARBBANI SAHAY GUHA SIRCAR.

IN continuation of the work on substituted paraconic acids (J., 1927, 1257) systems of a still simpler nature have been studied. Although the literature on lactones is fairly extensive, many of the methods described therein are unsuitable for the preparation of the β-mono- and ββ-di-substituted lactones that are necessary to bring the present work into line with the author's previous work on the substituted succin- and glutar-imides (J., 1927, 600, 1252). For instance, reduction of the chlorides or anhydrides of dibasic acids with sodium or aluminium amalgam (Saytzeff, Fichter) generally gives unsatisfactory yields (5—20%). The methods employing γ- and δ-halogenated butyric and valeric acids (Funk, Henry, Cloves) are inapplicable to the higher members of the series owing to the difficulty of preparing suitable halogen compounds. The βγ- and γδ-unsaturated acids (Fittig, Hjelt) corresponding to β-*spiro*-substituted lactones are again obviously unrealisable. The use of acetoacetic or malonic ester (Traube, Wolff, Marburg) is also inexpedient. Reduction of the readily accessible anhydrides of succinic and glutaric acids has its limitations, for the unsymmetrically substituted succinic acids give a difficultly separable mixture of

the α- and β-substituted lactones produced by reduction of one or other of the two carbonyl groups (Blanc, *Compt. rend.*, 1904, **139**, 1213).

A general method for the preparation of β-substituted butyrolactones consists in heating the dry silver salt of a glutaric acid with iodine, a mixture of the acid anhydride and the lactone with one carbon atom less than the original acid being formed (Windaus, *Ber.*, 1921, **54**, 581):



The yield of lactone is 30—40%, and since a good part of the anhydride can be recovered as the acid and used again, this method has been utilised in the present instance to prepare simple and mono- and di-substituted butyrolactones.

The substituted valerolactones are best prepared by reduction of the corresponding glutaric anhydrides with sodium and absolute alcohol; sodium amalgam, aluminium amalgam, and zinc dust and acetic or hydrochloric acid give less satisfactory results.

The substituents present in the series of lactones thus prepared are: H, H; Me, H; Et, H; Me, Me; Me, Et; Et, Et; *cyclo*pentane; *cyclo*hexane. The application of the valerolactones in preparing β-substituted adipic acids and the corresponding *cyclo*pentanones is reserved for a future communication.

One method of comparing the stabilities of the two series of lactones would be the determination of their velocity of formation from the hydroxy-acids by means of hydrochloric acid (compare Hjelt, *Ber.*, 1896, **29**, 1855). This method, however, is inapplicable on account of the extreme ease of lactone formation from the higher hydroxy-acids. Henry's method (*Z. physikal. Chem.*, 1892, **10**, 96), therefore, was used, the velocity of hydrolysis of the lactones in $N/200$-solution in 25% ethyl alcohol by the equivalent quantity of alkali hydroxide being determined on the assumption that the reactions are bimolecular.

The results (see table) show that, although the tendency is towards greater stability as each series of lactones is ascended, there are one or two important deviations. For instance, the greatest stability is shown by diethylbutyrolactone in the first series and by *cyclo*pentane*spiro*valerolactone in the second series.

	Butyrolactones.		Valerolactones.	
Substituents.	Limits of $k \times 10^5$.	Mean $k \times 10^5$.	Limits of $k \times 10^5$.	Mean $k \times 10^5$.
H, H	2660—2870	2790	1470—1570	1520
Me, H	1550—1660	1600	1610—1710	1660
Et, H	1760—1920	1820	1000—1770	1330
Me, Me	460— 524	483	428— 562	494
Me, Et	400— 444	422	350— 399	378
Et, Et	380— 426	415	190— 250	220
*cyclo*Pentane	500— 568	504	126— 133	129
*cyclo*Hexane	470— 541	506	322— 359	340

The number of determinations was 5—7 in each case.

From the results described here and in previous papers, it seems reasonable to conclude that, though the influence of substituents is generally exerted in the direction of increasing stabilisation of the molecule towards hydrolysing agents, it is not easy to predict at what point of any one series the maximum stability will be reached. There seems to exist in each particular class of compounds an optimum condition of stability which is reached by a certain member, the other members falling away from this ideal state according to the extent to which the substituents present in them fail to relieve the strain in the molecular framework. If, as in the present series, the first or the unsubstituted member is in a condition of maximum strain, the tendency of more and more bulky substituents would naturally be to relieve the strain with better and better effect, till the optimum stability is reached. After this, the introduction of still bulkier substituents, or the further forcing together of the extracyclic bonds by the influence of a ring attached to the other bonds of the central carbon atom, can diminish the stability only by straining the bonds of the oxygen atom from the position of greatest stereochemical "ease." A similar case of the reversal of the anticipated effect of substituents was noticed by Dickens, Kon, and Thorpe (J., 1922, **121**, 1496) in the formation of the *cyclo*pentanedione ring by the condensation of oxalic ester with substituted glutaric esters. It was there found that, as the glutaric series was ascended, the difficulty of ring formation was increased owing to the overlapping of the ends of the intermediate open chain (of the oxalyl derivative) brought about by the substituents.

Experimental.

Preparation of the Butyrolactones.—The silver salts of the glutaric acids (precipitated in 80—90% yield by the usual method) crystallised from much boiling water in needles, without appreciable decomposition. They were dried in the steam-oven for 12 hours, finely powdered, and mixed thoroughly with fine sand (3 parts) and then with iodine (1·1 equivs.). The mixtures were each heated at

100—150° for 1—1½ *hours and the cooled product was exhaustively* extracted with ether. The extract was concentrated somewhat, shaken with a saturated solution of potassium carbonate containing a little sodium sulphite, to remove the anhydride and most of the iodine (in the case of the higher members dilute alkali can be used with advantage, as the anhydrides are somewhat stable; removal of iodine is also thus facilitated), dried with potassium carbonate, *and distilled. A small quantity of iodine in the distillate can be* removed by means of mercury, but if the amount is considerable the distillate is diluted with ether and the washing is repeated, before distillation of the lactone under reduced pressure.

In each case the structure of the lactone was proved by oxidising 0·5—1·0 g. of it with a mixture of 2 g. of potassium dichromate and 40 c.c. of 10% sulphuric acid on the steam-bath for 3—5 hours. The *succinic acid corresponding to the lactone was obtained in very* good yield and it was directly compared (mixed melting point) with a genuine specimen.

The lactones are colourless, mobile, pleasant-smelling liquids (except the dimethyl compound, m. p. 57—58°). The lower members are completely miscible with water, but the solubility gradually diminishes and the boiling point increases as the series is ascended.

Butyrolactone was obtained in 30% yield from glutaric acid; b. p. 206°, or 89°/12 mm. (Windaus, *loc. cit.*, gives b. p. 203°) (Fonnd: C, 55·6; H, 7·1; Ag, in silver salt, 51·2. Calc.: C, 55·8; H, 7·0; Ag, 51·2%).

β-*Methylbutyrolactone* was obtained in 35% yield from β-methylglutaric acid; b. p. 88°/12 mm. (Found: C, 59·35; H, 7·85. $C_5H_8O_2$ requires C, 60·0; H, 8·0%. Found for the *silver* salt: Ag, 47·8. $C_5H_9O_3Ag$ requires Ag, 48·0%).

β-*Ethylbutyrolactone* (40% yield) has b. p. 99°/12 mm. (Found: C, 63·05; H, 8·65. $C_6H_{10}O_2$ requires C, 63·15; H, 8·8%. Found for the *silver* salt: Ag, 45·05. $C_6H_{11}O_3Ag$ requires Ag, 45·2%).

ββ-Dimethylbutyrolactone (30% yield) has b. p. 206°, or 89°/12 mm. It solidifies in the receiver and then has m. p. 55—56°. Windaus records b. p. 207—208° and m. p. 55—57° (Found: C, 63·1; H, 9·0; Ag, in silver salt, 44·9. Calc.: C, 63·15; H, 8·8; Ag, 45·2%).

β-*Methyl*-β-*ethylbutyrolactone* (40% yield) has b. p. 98°/10 mm. (Found: C, 65·3; H, 8·95. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%. Found for the *silver* salt: Ag, 42·6. $C_7H_{13}O_3Ag$ requires Ag, 42·7%).

ββ-*Diethylbutyrolactone* (50% yield) has b. p. 117°/12 mm. (Found: C, 67·35; H, 9·6. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%. Found for the *silver* salt: Ag, 40·4. $C_8H_{15}O_3Ag$ requires Ag, 40·75%).

β-cyclo*Pentane*spiro*butyrolactone* was obtained in 20% yield from *cyclo*pentanediacetic acid; b. p. 120—121°/11 mm. (Found: C, 67·5; H, 8·6. $C_8H_{12}O_2$ requires C, 67·6; H, 8·6%. Found for the *silver* salt: Ag, 40·7. $C_8H_{13}O_3Ag$ requires Ag, 40·75%). On oxidation it gave *cyclo*pentane-1-carboxy-1-acetic acid, m. p. 158—159°.

β-cyclo*Hexane*spiro*butyrolactone*, obtained in 45% yield from the corresponding diacetic acid, has b. p. 138°/11 mm. (Found: C, 70·0; H, 9·2. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1. Found for the *silver* salt: Ag, 38·6. $C_9H_{15}O_3Ag$ requires Ag, 38·7%). On oxidation it gave *cyclo*hexane-1-carboxy-1-acetic acid, m. p. 132°.

Preparation of the Valerolactones.—The requisite glutaric anhydrides were obtained in 80—90% yield by boiling the acid (1 mol.) with acetic anhydride (2·5 mols.) and distilling the product under reduced pressure; they collected in the receiver as colourless liquids which rapidly solidified. Care is necessary in distilling dimethylglutaric anhydride, which melts at 124° and tends to block the outlet tube during distillation. Rapid boiling and the use of not very low pressure, or distillation from a retort at ordinary pressure, avoids this difficulty.

The anhydride (1 mol.) is reduced in boiling absolute alcohol (10 mols). by the gradual addition of sodium (4 mols.; twice the theoretical quantity). The cooled mixture is decomposed with water, the alcohol distilled in steam, and the residue acidified with hydrochloric acid and refluxed for 10 minutes to complete the lactone formation; it is then cooled and repeatedly extracted with pure ether. The ethereal solution is washed free from acid (a good proportion of the unchanged glutaric acid may be recovered from the washings), dried over potassium carbonate, and distilled. The residue after removal of ether gave the lactone as the main product in 25—45% yield, together with a small lower-boiling fraction containing the glycol (compare Blanc, *loc. cit.*).

On oxidation with chromic acid each lactone gave the corresponding glutaric acid.

Valerolactone was obtained from glutaric anhydride in 25% yield; b. p. 114°/17 mm. After several weeks the b. p. rises, owing no doubt to partial polymerisation (Found: C, 59·95; H, 8·3; Ag, in silver salt, 47·9. Calc.: C, 60·0; H, 8·0; Ag, 48·0%).

β-*Methylvalerolactone* was obtained from β-methylglutaric anhydride in 25% yield; b. p. 90°/12 mm. (Found: C, 62·85; H, 8·65. $C_6H_{10}O_2$ requires C, 63·15; H, 8·8%. Found for the *silver* salt: Ag, 44·9. $C_6H_{11}O_3Ag$ requires Ag, 45·2%).

β-*Ethylvalerolactone* (28% yield) has b. p. 104°/13 mm. (Found:

C, 65·5; H, 9·5. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%. Found for the *silver* salt: Ag, 42·45. $C_7H_{13}O_3Ag$ requires Ag, 42·7%).

ββ-Dimethylvalerolactone (30% yield) has b. p. 108°/12 mm. and m. p. 30°. Blanc (*loc. cit.*) gives b. p. 232—233° and m. p. 30° (Found: C, 65·4; H, 9·4; Ag, in silver salt, 42·85. Calc.: C, 65·6; H, 9·4; Ag, 42·7%).

β-*Methyl*-β-*ethylvalerolactone* (30% yield) has b. p. 122°/10 mm. (Found: C, 67·5; H, 9·6. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%. Found for the *silver* salt: Ag, 40·25. $C_8H_{15}O_3Ag$ requires Ag, 40·45%).

ββ-*Diethylvalerolactone* (50% yield) has b. p. 143—144°/15 mm. (Found: C, 69·05; H, 10·05. $C_9H_{16}O_2$ requires C, 69·2; H, 10·25%. Found for the *silver* salt: Ag, 38·55. $C_9H_{17}O_3Ag$ requires Ag, 38·4%).

β-cyclo*Pentane*spiro*valerolactone* was obtained in 30% yield from the anhydride (b. p. 176—178°/12 mm., m. p. 68°); b. p. 146°/12 mm. (Found: C, 69·8; H, 9·1. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%. Found for the *silver* salt: Ag, 38·8. $C_9H_{15}O_3Ag$ requires Ag, 38·7%).

β-cyclo*Hexane*spiro*valerolactone* was obtained in 35% yield from the anhydride (b. p. 186°/15 mm., m. p. 73°); b. p. 158—159°/10 mm. (Found: C, 71·4; H, 9·25. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%. Found for the *silver* salt: Ag, 36·8. $C_{10}H_{15}O_3Ag$ requires Ag, 36·9%).

Hydrolysis.—The hydrolysis constants of the lactones in *N*/200-solution at 25° in the presence of an equivalent quantity of sodium hydroxide were determined as described in Parts I and II (*loc. cit.*), the only difference being the employment of 25% alcohol (by volume) for making up the solutions, as the higher members were found to be sparingly soluble in water at the dilution employed. In the presence of alcohol the velocity coefficients are higher than when water alone is used, the value for butyrolactone, for example, being 0·0279 instead of 0·0253 as obtained by Henry.

The author wishes to express his thanks to Professor J. F. Thorpe, C.B.E., D.Sc., F.R.S., for his kind interest in this work, and to the Chemical Society for a grant that defrayed a part of its cost.

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CXXI.—*Mobile-anion Tautomerism. Part I. A Preliminary Study of the Conditions of Activation of the Three-carbon System, and a Discussion of the Results in Relation to the Modes of Addition to Conjugated Systems.*

By HAROLD BURTON and CHRISTOPHER KELK INGOLD.

ONE of the advantages which accrue from the interpretation of the reactions of Organic Chemistry in the light of the electronic theory of valency is that similar laws are seen to govern apparently diverse types of phenomena, such as mobility and equilibrium in tautomeric systems and orientation in aromatic substitution. Thus in the field of prototropic change, the dependence of mobility on the ionising properties of the system as exhibited by the stability of its sodium and potassium salts was already recognised (Ingold and Piggott, J., 1922, 2381); but the application of the electronic theory showed also that groups which contribute to the stability of the electromeric anion act as they do owing to their affinity for the negative charge, which circumstance renders the same groups strongly *m*-orienting in aromatic substitution: a correct interpretation of the mechanism of the two phenomena renders the agreement complete (Ingold, Shoppee, and Thorpe, J., 1926, 1477; Cooper and Ingold, J., 1927, 836).

It can be seen in a general way that opposite conditions will prevail in mobile-anion tautomerism (anionotropy), and that a somewhat similar parallelism should subsist between the power of groups to confer mobility and their *op*-directing efficiency in aromatic substitution; thus may the greater stability of the ionised salts of nitrogen- than of oxygen-pseudo-bases be correlated with the greater *op*-directing power of ·NRR′ than of ·OR. At the same time, certain differences would be expected, so that it would be false to invert mechanically all conclusions relating to the previous comparison. As to this point, an example will make our meaning clear.

The conferment of prototropic mobility by the groups $\cdot SO_2R$ and ·NR′R″R‴ is at present being studied in these laboratories and the complete results are not yet available, but on theoretical grounds it is not to be expected that these groups, despite their great *m*-orienting power, would confer a correspondingly greater degree of mobility on an attached three-carbon system than ·COMe, for example; for although the groups $\cdot NR_3$, etc., must attract electrons very strongly, they cannot provide a seat for the anionic charge without expanding an already-filled, stable electron group,

or commencing a new group; they might, however, act indirectly by increasing the toleration of an adjacent carbon atom for a lone-pair. Thus in the conferment of prototropic mobility, $\cdot NR_3$ and $\cdot COR$ necessarily act by different mechanisms, whereas in *m*-orientation they act, mainly at any rate, by an identical mechanism (Ingold and Shaw's "Case 2," J., 1927, 2918; compare Cooper and Ingold, *loc. cit.*; Baker, Cooper, and Ingold, this vol., p. 429); therefore we cannot equate their effects in the two cases. Now in the realm of anionotropy there is a corresponding difference between the functions of the activating groups $\cdot CH_3$ and $\cdot OR$: the former may repel electrons (as compared with $\cdot H$) and so increase the toleration of an adjacent carbon atom for a shared sextet, but it cannot without disruption provide a seat for the cationic charge; the latter group, on the other hand, can readily do so by sharing one of its lone-pairs. A precisely similar difference of mechanism relates to the *op*-orienting behaviour of these groups in aromatic substitution (Ingold and Shaw's "Cases 1" and "3"). Thus the connexion between anionotropy and *op*-orientation should be of a simpler and more direct kind than the previously studied connexion between prototropy and *m*-orientation.

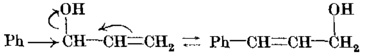
These considerations led us to embark upon a general investigation on the effect of groups in promoting anionotropic change, and in this paper some preliminary results are given for the systems

$$Ar\cdot CHX\cdot CH{:}CH_2 \rightleftharpoons Ar\cdot CH{:}CH\cdot CH_2X$$
$$Ar\cdot CHX\cdot CH{:}CHAr' \rightleftharpoons Ar\cdot CH{:}CH\cdot CHX\cdot Ar'$$

where the potentially mobile anion, X, is OR or Hal. Gillet appears to have been the first (*Bull. Soc. chim. Belg.*, 1922, **31**, 366) to direct attention to the significance of polar factors in three-carbon anionotropy, and to have suggested what is undoubtedly a correct partial explanation of 1 : 4-addition of halogens, namely, that 1 : 2-addition is succeeded by anionotropic change (compare Prévost, *Compt. rend.*, 1927, **184**, 1460; Farmer, Laroia, Switz, and Thorpe, J., 1927, 2937; Farmer, Lawrence, and Thorpe, this vol., p. 729). Gillet formulates his conclusions as follows: "If in the system $\overset{1}{C}{=}\overset{2}{C}{-}\overset{3}{C}(X)$ the radicals at C_3 are as a whole more negative than those at C_1, the most negative radical (X) attached to C_3 will tend to migrate to C_1." This view at once led its author into difficulties, however, for in the majority of available examples an alkyl group attached to C_3 appeared to be the predominating factor determining the departure of X. Thus Gillet was forced to draw a distinction between "migrations vraies" (those which followed his rule), and "transpositions hydrolytiques" (those

which did *not*). The latter were regarded as dependent on the preliminary addition of water or some other addendum to the double bond and subsequent fission in another direction—despite the fact that there is no clear distinction between the conditions of occurrence of the change in two series of cases, and that these conditions are frequently such as to render the addition-and-elimination theory extremely improbable. Reference may also be made to a recent paper by Prévost (*Compt. rend.*, 1927, **185**, 132), who, following up Lowry's explanation of prototropy (*Deuxième Conseil de Chimie, Congrès Solvay*, 1925, p. 156), applies to anionotropy the theory of alternate polarities in the extreme form in which the carbon double bond is regarded as semi-polar; this conception, however, does not enable Prévost to advance the problem of elucidating the structural conditions under which anionotropy is manifested.

In the system :

(I.)  (II.)

the degree of mobility is not very great, for the two alcohols can be obtained as separate individuals and we have prepared from each a crystalline *p*-nitrobenzoyl derivative. It is true that Valeur and Luce (*Bull. Soc. chim.*, 1920, **27**, 611) claim to have transformed (I) into (II) by means of dilute sulphuric acid, but we have not succeeded in repeating this observation, and, without controverting it, may state that our numerous attempts have given us the impression that it would be very difficult to effect a *smooth* conversion in the manner indicated. On the other hand, we find that the alcohol (I) is smoothly and completely converted into the acetate of (II) by boiling with acetic anhydride. Furthermore, Moureu and Gallacher (*ibid.*, 1921, **29**, 1059) obtained from the two alcohols the same crystalline bromide, which, they surmised, was cinnamyl bromide; and we have proved the correctness of this structure by ozonolysis, wherehy benzoic acid and hromoacetaldehyde were obtained. The *p*-tolyl analogues of (I) and (II) can also exist separately, but the former is converted by acetic anhydride into the acetate of the latter easily and completely with no indication of perceptible reversibility. The reaction is more facile than in the phenyl series. Smooth conversion into substituted cinnamyl bromides occurs when the *p*-tolyl analogues of (I) are treated with cold hydrogen bromide in acetic acid solution. It would, of course, be expected that the tendency to migration of different potentially mobile anions (X) contained in systems otherwise identical would follow the order of anionic stability (strengths of the acids HX), as,

for example, OH < OAc < Br. Further it follows from the presumed influence (represented by ⟶ in I) of the aryl group in increasing the toleration of C_a for the shared sextet left on separation of $\overset{\ominus}{OH}$, that the equilibrium in systems such as I ⇌ II should strongly favour form II, the more so the stronger the activation by Ar— and this is undoubtedly the case. On the other hand, there is evidence that in systems of the form

$$\text{(III.)}\quad Me \longrightarrow \underset{}{\overset{OH}{CH}}{-}CH{=}CH_2 \rightleftharpoons Me{-}CH{=}CH{-}\overset{OH}{CH_2}\quad \text{(IV.)}$$

not only is the mobility less, but also there is a less uneven relation between the forms at equilibrium. Thus Baudrengheim found (*Bull. Soc. chim. Belg.*, 1922, **31**, 160) that each alcohol yielded its own acetyl derivative on boiling with acetic anhydride, although *a slight interconversion in the sense III⟶IV was observed when* a mixture of acetic anhydride and sulphuric acid was used. Furthermore, both alcohols yielded an equilibrium mixture of isomeric chlorides, in which, although the chloride of (IV) was certainly the main constituent, the chloride of (III) was present in sufficient amount to enable it to be separated by distillation. Both these comparisons with the phenyl case are consistent with the view that the phenyl gronp with its looser electronic system can more completely neutralise the positive charge left on C_a by the separation of the anion than can the methyl group. Comparison with the effect of phenyl in promoting the formation of styrene from β-phenylethylammonium salts (Hanhart and Ingold, J., 1927, 997) establishes yet another point. In this reaction the phenyl neutralises the negative charge left on carbon by the separation of a cation (hydrogen). It follows that in both cases the *primary* change is the ionisation (—OH, above), and that the action of the facilitating group (⟶ above) is a compensating, not an initiating, process.*

For the investigation of the αγ-diarylated systems we have employed two methods of diagnosis, one of which, namely, ozonolysis, needs no explanation. The other depends on the prototropic change exemplified by

$$C_6H_5{\cdot}CH(OH){\cdot}CH{:}CH_2 \longrightarrow C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_3$$

(Tiffeneau, *Bull. Soc. chim.*, 1907, **1**, 1209) and

$$C_6H_5{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C_6H_5 \longrightarrow C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$$

* The power of the phenyl group (which is enhanced in *p*-diphenylyl and other polynuclear groups) to compensate electrostatic disturbances of either sign in an attached atom is doubtless the cause of the dissociability of the hexa-arylethanes and allied compounds.

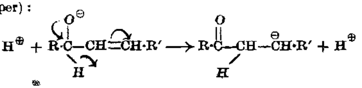
(Nomura, *ibid.*, 1925, **37**, 1245). These reactions take place quantitatively in the presence of alcoholic alkali,* and the ketones formed can readily be synthesised by adaptations of the acetoacetic ester method, and thus identified. The first of the examples cited above shows that hydroxyl-migration does not precede the prototropic change, and confirmation of this is to be found in experiments described below; nor would a preliminary change of this kind be expected, since the catalyst (alkali) is essentially one for promoting *cationotropic* change (Ingold, Shoppee, and Thorpe, *loc. cit.*).

Our principal object in this part of the investigation was to obtain a *comparison of the activating effects* of the *groups* $p\text{-}CH_3{\cdot}C_6H_4-$ and $p\text{-}Cl{\cdot}C_6H_4-$, since only the latter contains unshared electrons by the sharing of which a seat can be provided for the positive charge on the electromeric cation. No difficulty was experienced in preparing (by the usual Grignard method) the member (V) of the system

$$\text{(V.)}\ (p)\ Me{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}C_6H_5 \rightleftharpoons (p)\ Me{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH(OH){\cdot}C_6H_5\ \text{(VI.)}$$

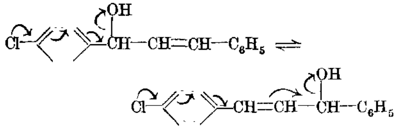
It was crystalline, and showed no tendency to pass into its isomeride (VI). Re-arrangement with alcoholic alkali yielded exclusively the crystalline ketone $(p)\ Me{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$, which was synthesised *via* ethyl α-benzyl-*p*-toluoylacetate. On the other hand, the acetate prepared from (V) with acetic anhydride was *manifestly an equilibrium mixture*: with alkalis it yielded a mixture of the ketones $C_7H_7{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$ and $C_7H_7{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$ (both synthesised) probably containing an excess of the latter, although our separation was not sufficiently complete to enable us to assert this definitely; furthermore, ozonolysis of the acetates, followed by hydrolysis of the ozonides, yielded considerable quantities of *p*-tolualdehyde, *p*-toluic acid, and mandelic acid, and smaller quantities of benzoic acid and a very soluble acid which was probably *p*-methylmandelic acid because on further oxidation it gave *p*-toluic acid. That the equilibrium is probably in favour of the acetate of (VI) is, of course, consistent with the anticipated *greater effect of* $CH_3{\rightarrow}C_6H_4{\rightarrow}C^\alpha$ *than of* $H{-}C_6H_4{\rightarrow}C^\alpha$ *in* compensating for the loosening of the anion from its attachment to C_α. On the other hand, in the *p*-chloro-series, not only the acetates,

* They probably take place through the anion by the "pinacolic" electron-displacement (see Ingold and Shoppee, this vol., p. 365; Shoppee, forthcoming paper):



ut also the alcohols themselves, passed into an equilibrium mixture, o that we were unable to obtain the individuals (VII) and (VIII) eparately :

(VII.)

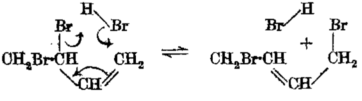


(VIII.)

n this case, the indications were clearly that (VIII) is the aain isomeride. Treatment with alkali yielded a large pro-ortion of p-$Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$ and a small amount of -$Cl{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_5$ (both synthesised), and hydrolysis of he mixed ozonides gave p-chlorobenzoic and mandelic acids in arge quantity, together with a little benzoic acid, and a very oluble acid presumed to be p-chloromandelic acid from its oxidation o p-chlorobenzoic acid.

Thus the order of facilitation of three-carbon anionotropy by -substituents is p-$Cl{\cdot}C_6H_4{\cdot} \gg p$-$Me{\cdot}C_6H_4{\cdot} > C_6H_5{\cdot} \gg CH_3{\cdot} > H$; which grees, as it theoretically should, with the op-orienting sequence l$>$Me$>$H as inferred in the ordinary way from the proportions of someride formed in benzene substitutions.

As regards the function of catalysts, these must obviously be of uch a kind that they have a sufficient affinity for the mobile group. cids (*e.g.*, HBr, H_2SO_4) might act in this way (either directly or *ia* the hydronium ion), as also might polarised or readily polarisable rgauic compounds such as acid anhydrides (*e.g.*, Ac_2O). As to the recise history of the eliminated anion, we are prepared at present o entertain two views; either (as is assumed above) it may leave he molecule completely in covalent or molecular combination with he catalyst, to be subsequently returned to another molecule in ne of the two possible positions of reunion; or, in certain cases, oncomitantly with the elimination (ionisation) of the group, its quivalent may be introduced into the new position by an internal yclic process such as



Ve hope at a later date to be able to submit further evidence on his question.

Addition to Conjugated Systems.

Although Thiele's writings leave little room for doubt that he originally intended his hypothesis to imply universal 1 : 4-addition in conjugated systems of two double linkings, it has long been known that this position cannot be maintained, so that the Thiele hypothesis, even with its later extensions, has not the diagnostic value which it was once imagined to possess. In short, there exists no theory of orientation in additions to conjugated unsaturated systems comparable in range and definition with the orientation theory which has been developed for substitutions in aromatic systems. Chandrasena and Ingold (J., 1922, **121**, 1306) formulated certain rules for conjugative additions, but these rules were avowedly empirical, and it is our view that they require supersession. The provision of data for the development of this subject on more fundamental lines has been one of the major objects of the investigation outlined above.

The subject divides itself into three main parts according to the nature of the addendum, and then into sub-sections depending on the structure of the unsaturated complex. The general scheme of classification * may be indicated as follows :—

Case 1. Both parts of addendum stable as anions (Cl_2, Br_2, ICl, OHCl, etc.). Structural influences (*a*) favour, (*b*) inhibit, anionotropic mobility.

Case 2. One part of addendum stable as anion, and the other as cation [HBr, HCl, HCN, $NH_2{\cdot}OH$, $CH_3{\cdot}NO_2$, $CH_2(CO_2Et)_2$, etc.]. Structural influences (*a*) favour, (*b*) inhibit, anionotropic mobility.

Case 3. Both parts of addendum stable as cations (H_2).

In this paper it is proposed to deal only with Cases 1*a* and 2*a*, because it is to these that the new experimental material primarily relates. Our general theoretical method will be fairly obvious from the examples taken, but we prefer to postpone actual discussion of the remaining four divisions of the subject until the experimental work appropriate to them has been completed.†

Case 1*a. Example : Addition of Bromine to Conjugated Unsaturated Hydrocarbons.*—In any given instance two questions arise,

* This must be interpreted with due care, and two possible pitfalls may be indicated. (1) If a group retards one kind of tautomeric change, it seems safe to assume that it will promote the other; but the converse does not necessarily hold, as is indicated by the example on p. 907. (2) Although a group will normally exhibit greater stability as one kind of ion, special structural conditions may reverse its rôle; thus we hold that bromine is a potential cation in $CH_3{\cdot}CO{\cdot}CHBr{\cdot}CO_2Et \longrightarrow CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$, though we are aware that contrary views have been expressed.

† For partial statement of application to Case 3 see *Chem. and Ind.*, 1928, 47, 980

one of which is more remote than the other. The less remote, and *practically* more important, question is : What is the *stable* product ? For in the case under consideration, only potentially mobile anions are introduced by the addendum, and the groups already present favour anionotropic change; it follows that unless special experi*mental precautions are taken the stable product will be the one* isolated. A theoretically interesting, but much more difficult question is : What is the *initial* product ? This will be considered afterwards.

The stable product. To discover this by the method to be given, the simplest plan is to make an assumption as to the structure of the initial product. We shall suppose that a 1 : 2-dibromide is first formed. The accuracy of this assumption will be considered later, when it will also appear that it is not important for the purpose in view that it should be accurate.

Butadiene. Let it be assumed that $CH_2Br{\cdot}\overbrace{CHBr{\cdot}CH{:}CH_2}$ is first formed. The bracket indicates the anionotropic system, and the activating group is ·CH_2Br, which, by analogy with ·CH_2Cl, must be a very weak *op*-orienting group—weaker than ·CH_3 and therefore not incomparable with ·H. Anionotropic change to the 1 : 4-product will therefore (compare activation by CH_3, p. 907) be notably incomplete and we should expect a substantial amount of 1 : 2-by-product to accompany the 1 : 4-main product. [Farmer, Lawrence, and Thorpe find 1 : 2-dibromide 30%, 1 : 4-dibromide 70% on bromination with bromine in acetic acid at 4° (*loc. cit.*).]

Isoprene. Here an additional methyl group is present to promote the change $\genfrac{}{}{0pt}{}{CH_3}{CH_2Br}\!\!>\!\overbrace{CBr{\cdot}CH{:}CH_2} \longrightarrow \genfrac{}{}{0pt}{}{CH_3}{CH_2Br}\!\!>\!C{:}CH{\cdot}CH_2Br$, so that the proportion of 1 : 4-dibromide should be somewhat higher than in butadiene [Staudinger, Muntwyler, and Kupfer find that isoprene dibromide, which is a liquid, consists mainly of the 1 : 4-compound, but the precise proportion is not known (*Helv. Chim. Acta*, 1922, **5**, 756).] (*A*).

βγ-Dimethylbutadiene. For similar reasons, the proportion of 1 : 4-compound should be higher than in butadiene. [The recorded data (Kondakow, *J. pr. Chem.*, 1900, **62**, 171) do not appear to be inconsistent with this inference, despite the interpretation given in Beilstein's " Organische Chemie " (4te Aufl., I, 218) in which the dibromide is assigned a 1 : 2-formula.]

αδ-Diphenylbutadiene. If $Ph{\cdot}CHBr{\cdot}\overbrace{CHBr{\cdot}CH{:}CH}{\cdot}Ph$ were first formed, the relatively slow and incomplete change (promoted by $Ph{\cdot}CHBr{\cdot}$) to the isomeride $Ph{\cdot}CHBr{\cdot}\overbrace{CH{:}CH{\cdot}CHBr}{\cdot}Ph$ would be immediately succeeded by the much more rapid and complete

change (promoted by Ph·) to Ph·CH:CH·CHBr·CHBr·Ph (compare anionotropic changes promoted by Ph; p. 906). Hence the main product should be the 1 : 2-(= 3 : 4-)dibromide. [This has been established by Strauss (*Ber.*, 1909, **42**, 2867).] (*B*).

a-Phenylbutadiene. Similar considerations show that the main product should be Ph·CH:CH·CHBr·CH_2Br. [Strauss has demonstrated this also (*loc. cit.*, p. 2871).]

Hexatriene. Since vinyl is expected to act like phenyl, the 3 : 4- and 1 : 4-dibromides will not be obtained as stable products, since the former would be comparatively slowly and reversibly transformed into the latter, whilst this would pass rapidly and substantially completely, either into the 1 : 2-isomeride (change facilitated by ·CH:CH_2), or into the 1 : 6-compound (change facilitated by ·CH:CH·CH_2Br). [Farmer, Laroia, Switz, and Thorpe obtained 1 : 2- from *cis*-hexatriene and 1 : 6- from *trans*-, but did not in either case encounter 1 : 4- or 3 : 4- (*loc. cit.*).]

αζ-Diphenylhexatriene. The dibromide should be either 1 : 2- or 3 : 4-, but not 1 : 4- or 1 : 6-. (It has not yet been oriented.)

The initial product. The above provisional hypothesis tha 1 : 2-addition precedes the formation of a 1 : 4-dibromide require consideration. The work of Orton and King (J., 1911, **109**, 1369 and Soper and Smith (J., 1926, 1582) shows that in chlorine-sub stitution, either by Cl_2 or by HOCl, the molecule, and not either c its ions, is the actual reagent, even in an ionising solvent such a water : it may be assumed that the same is true for halogen additio in all ordinary circumstances. In the light of this conclusion, th experiments of Terry and Eichelberger (*J. Amer. Chem. Soc.*, 192 **47**, 1067) and of Francis (*ibid.*, p. 2340) are seen to prove that th halogen molecule initially supplies only one halogen atom to th unsaturated substance; thus, to quote one experiment, the secon stage of the presumed mechanism

$$CH_2{:}CH_2 + Br_2 \longrightarrow CH_2Br{\cdot}CH_2^{\oplus} + Br^{\ominus} \longrightarrow CH_2Br{\cdot}CH_2Br$$

may be modified by using bromine water containing a solul nitrate; the nitrate ion then competes with the bromide ion a $CH_2Br{\cdot}CH_2{\cdot}O{\cdot}NO_2$ is formed along with $CH_2Br{\cdot}CH_2Br$. Tl demonstration applies, however, only to conditions favouri ionisation, and it is not to be expected that under non-ionisi conditions a free halide ion would be liberated. Under such co ditions the initial product of addition to a conjugated system co only be a 1 : 2-compound, and an elegant demonstration of this l been given by Thorpe and Farmer in the work already quoted. the other hand, under conditions favourable to ionisation a proc analogous to that depicted for ethylene might occur, so that

initial product would more correctly be described as consisting of the ions of the 1 : 2-dibromide. We have, however, already (p. 909) entertained the hypothesis that in an anionotropic change, such as 1 : 2-dibromide ⟶ 1 : 4-dibromide, ionisation (not *necessarily* dissociation) precedes the electromeric transformation, and if the ions are pre-formed, the mechanism is simplified to that extent. Thus the object of this paragraph is to point out that our actual view of the general case, namely, Reagents ⟶

$$\text{Ions of } 1:2\text{-bromide} \begin{cases} \rightleftharpoons 1:2\text{-Bromide} \\ \searrow \text{Ions of } 1:4\text{-bromide} \rightleftharpoons 1:4\text{-Bromide} \end{cases}$$

remains consistent with the results obtained by the use of the simplified hypothetical mechanism.

Case 2a. Examples: Additions of Hydrogen Bromide and Hydrogen Cyanide to Conjugated Unsaturated Acids and Esters, and Michael's Addition Reaction.—The potentially mobile cation (hydrogen) may be assumed to enter *via* the carbonyl oxygen; its final position will normally be the α-position unless the conditions are suitable for the αβ–βγ-prototropic change (Kon, Linstead). The position of stability of the mobile anion is of more interest in relation to the experimental evidence submitted in this paper. That anionotropic change will control the situation is obvious in the case of hydrogen bromide-addition, and the reversibility of the Michael reaction, and its analogy with hydrogen cyanide-addition appears to guarantee that the same conclusion can be extended to these reactions.

The stable product. A few examples only will be mentioned, and for brevity the reasons for the theoretical conclusions which are given will be replaced by letters referring to some previous paragraph containing an argument sufficiently similar to the one omitted.

Sorbic acid and its esters. Lettering the butadiene chain as usual from the carboxyl group, both αβ- and αδ-addition would be expected, the potential anion being at C_β or C_δ (*A*). [The occurrence of αδ-addition of malonic ester has been established.]

Cinnamylideneacetic and cinnamylidenemalonic acids and their esters. Here *only* αβ-addition, and not αδ-addition, should occur, the anion going to C_β (*B*). [The addition of hydrogen bromide, and of malonic ester, to cinnamylideneacetic acid (or ester), and the addition of hydrogen bromide, hydrogen cyanide, and nitromethane to cinnamylidenemalonic acid (or ester), have been investigated. In all five cases, the products are those of αβ-addition.]

The initial product. The remarks under a corresponding heading relating to bromine-addition apply with a few obvious modifications to hydrogen bromide addition. The additions in alkaline solution

of hydrogen cyanide, malonic ester, etc., are, however, in a different category, and the question of the initial product does not seriously arise, since in general it will consist of the anions (formed simultaneously) of the two possible addition-products (Cooper and Ingold, J., 1926, 1868); the attachment of the cation, we assume, occurs subsequently (often during acidification).

Action of Phosphorus Pentachloride on αβ-Unsaturated Ketones and Related Reactions.

This subject is mentioned as another which receives satisfactory explanation on lines similar to those illustrated above. The reaction may be exemplified by $C_6H_5{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_5 \longrightarrow C_6H_5{\cdot}CCl{:}CH{\cdot}CHCl{\cdot}C_6H_5$, and the interpretation we should apply to the more complicated instances will be obvious to any who compare this paper with Strauss's original memoirs (*Annalen*, 1909, **370**, 315; 1910, **374**, 121; *Ber.*, 1910, **43**, 596; *Annalen*, 1912, **392**, 235; 1913, **401**, 121; 1918, **415**, 232; *J. pr. Chem.*, 1921, **103**, 1; *Annalen*, 1925, **442**, 93; **445**, 92). Thus in the dichlorohydrocarbon mentioned, one Cl is the potentially mobile anion, and the other functions like Cl in the *p*-chlorophenyl compounds referred to on p. 909.

EXPERIMENTAL.

α-Phenylallyl alcohol was obtained from acraldehyde and magnesium phenyl bromide as described by Moureu and Gallacher (*loc. cit.*). The p-*nitrobenzoate*, obtained (as an oil that solidified) by heating the alcohol (3·9 g.), pyridine (30 c.c.), and *p*-nitrobenzoyl chloride (5·9 g.) on the steam-bath for 15 hours and pouring the product into water, crystallised from alcohol in colourless plates m. p. 45—46° (Found: C, 68·1; H, 4·7. $C_{16}H_{13}O_4N$ requires C, 67·8; H, 4·6%). Cinnamyl *p*-nitrobenzoate, prepared similarly has m. p. 77—78° (compare Hill and Nason, *J. Amer. Chem. Soc.* 1924, **46**, 2215).

Conversion of α-Phenylallyl Alcohol into Cinnamyl Alcohol.—Reference has already been made to our failure to repeat Valeu and Luce's observation of direct interconversion; we used hot an cold sulphuric acid of various dilutions, and cold alcoholic hydr chloric acid, but obtained either unchanged material or produc of high and indefinite boiling point. A mixture of α-phenylall alcohol (5 g.) and acetic anhydride (5 c.c.) was boiled for 6 hou and then distilled. The acetate had b. p. 135—145°/15 mm., a its identity with cinnamyl acetate was confirmed by hydrolysis the crystalline alcohol under conditions in which the un-isomeris α-phenylallyl acetate became converted into phenyl ethyl ketor

It was boiled for 3 hours with 100 g. of 5% alcoholic potassium hydroxide, and the neutral hydrolysis product isolated in the usual way (4·5 g.); 0·5 g. of the ketone was obtained and the remainder was cinnamyl alcohol, b. p. 240—250°, m. p. 33°. A longer period of heating completes the reaction, which is not detectably reversible.

Bromide from α-Phenylallyl and Cinnamyl Alcohols.—This crystalline substance was readily obtained by adding the alcohol to an acetic acid solution of hydrogen bromide, but attempts to achieve the reverse reaction by means of moist silver oxide yielded complex mixtures, b. p. 80—300°/15 mm.; moreover, treatment with silver *p*-nitrobenzoate gave an amorphous solid, and ozonolysis was therefore resorted to. A chloroform solution of the bromide was treated with dry ozone for several days, and the oily ozonide decomposed by boiling with water into benzaldehyde (identified as semicarbazone) and bromoacetaldehyde (identified as bromal hydrate). Formaldehyde was not produced.

α-p-*Tolylallyl Alcohol*, $C_6H_4Me{\cdot}CH(OH){\cdot}CH{:}CH_2$.—The Grignard reagent prepared from magnesium (6 g.), *p*-bromotoluene (43 g.), ether (100 c.c.), and a trace of iodine was cooled below 0° and treated during 1·5 hours with a solution of acraldehyde (14 g.) in ether (72·5 c.c.). The mixture was well stirred for a further 3 hours and then decomposed by ice and dilute acetic acid. The oil obtained after extraction with ether, washing with sodium bicarbonate solution, drying, and evaporation was fractionated, and a fraction (20 g.), b. p. 120—122°/10 mm., collected; the remainder was *pp'*-ditolyl. The p-*nitrobenzoate*, prepared by the pyridine method, separated from alcohol in colourless, glistening plates, m. p. 82° (Found: C, 68·9; H, 5·25. $C_{17}H_{15}O_4N$ requires C, 68·7; H, 5·09%).

*Conversion of α-*p*-Tolylallyl Alcohol into 4-Methylcinnamyl Alcohol.*—This reaction was carried out as described on p. 914 but took place even more readily, the transformation to 4-methylcinnamyl acetate, b. p. about 140°/10 mm., being complete in 6 hours. The alcohol obtained by hydrolysis of the acetate at once solidified; m. p. 48°. A single crystallisation from ligroin yielded pure 4-*methylcinnamyl alcohol* as colourless, glistening plates, m. p. 51—52° (Found: C, 81·1; H, 8·05. $C_{10}H_{12}O$ requires C, 81·05; H, 8·2%). The p-*nitrobenzoate*, prepared by the pyridine method, crystallised from alcohol in almost colourless, prismatic needles, m. p. 131—132° (Found: C, 68·9; H, 5·2. $C_{17}H_{15}O_4N$ requires C, 68·7; H, 5·1%).

*Bromide from α-*p*-Tolylallyl Alcohol (4-Methylcinnamyl Bromide)*, $C_6H_4Me{\cdot}CH{:}CH{\cdot}CH_2Br$.—The bromide was prepared from the tolylallyl or 4-methylcinnamyl alcohol (8·2 g.) and a glacial acetic

acid solution of hydrogen bromide (30%; 50 g.). The bromide (10 g.) separated from acetic acid in colourless, glistening plates, m. p. 64—65° (Found: C, 56·9; H, 5·45. $C_{10}H_{11}Br$ requires C, 56·9; H, 5·25%). When this bromide was treated with silver *p*-nitrobenzoate in cold ethereal solution, an amorphous solid was obtained (Found: C, 66·9; H, 5·7%). The constitution of the bromide was determined by ozonolysis as in the previous example and with corresponding results.

Action of Bromine on αγ-Diphenylallyl Acetate.—αγ-Diphenylallyl alcohol was obtained by the action of cinnamaldehyde on magnesium phenyl bromide, and separated from petrol in long, silky needles, m. p. 58—59° (compare Nomura, *loc. cit.*). The acetate boils at 211°/15 mm. (Nomura gives b. p. 211°/9 mm.).

A solution of the acetate (5·7 g.) in cold carbon tetrachloride was treated with bromine (3·8 g.; a slight excess), also dissolved in carbon tetrachloride. The cold solution slowly deposited a *bromide* (3·9 g.), which crystallised from alcohol in colourless needles, m. p. 176—177° after previous softening (Found: C, 49·7; H, 3·7. $C_{17}H_{16}O_2Br_2$ requires C, 49·5; H, 3·9%). The mother-liquor from this bromide was evaporated to dryness, and the residual viscous oil dissolved in alcohol. A second *bromide* was slowly deposited (3·2 g.), which separated from alcohol in clusters of colourless slender needles, m. p. 122° (Found: C, 49·8; H, 3·95. $C_{17}H_{16}O_2Br_2$ requires C, 49·5; H, 3·9%). The residue (2·15 g.) was a viscous oil.

γ-Phenyl-α-p-tolylallyl Alcohol, $C_6H_4Me\cdot CH(OH)\cdot CH{:}CHPh$.—The Grignard reagent obtained from magnesium (6 g.), *p*-bromotoluene (43 g.), ether (100 c.c.), and a trace of iodine was treated at the ordinary temperature with a solution of cinnamaldehyde (33 g.) in ether (72·5 c.c.). The mixture was then boiled for 30 minutes and decomposed with ice and dilute acetic acid. The oil obtained from the ethereal extract, after being washed free from acid and dried partly solidified on standing. After draining, the solid residue (22 g.) crystallised from petrol in colourless needles, m. p. 78—79 (Found: C, 85·7; H, 6·9. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%).

Conversion into p-*tolyl β-phenylethyl ketone.* This *ketone* was obtained in almost quantitative yield by boiling the alcohol (3·5 g with alcoholic 20% potassium hydroxide (100 g.) for 2 hours and pouring the product into water. The oil obtained solidified and after being washed free from alkali, crystallised from alcohol in glistening plates, m. p. 70° (see p. 920).

Acetylation of γ-Phenyl-α-p-tolylallyl Alcohol. Formation of γ-Phenyl-α-p-tolylallyl Acetate and α-Phenyl-γ-p-tolylallyl Acetate.—A mixture of the pure alcohol (m. p. 78—79°) (15 g.) and acetic anhydride (15 c.c.) was boiled for 6 hours. After removal of the

excess of acetic anhydride, the residue distilled at 210—211°/11 mm. (Found: C, 80·9; H, 6·75. $C_{18}H_{16}O_2$ requires C, 81·2; H, 6·8%). That this constant-boiling liquid was a mixture of isomeric acetates was proved by hydrolysis and ozonisation.

Conversion into ketones. The acetate mixture (9 g.) and 20% alcoholic potassium hydroxide solution (150 g.) were boiled together for 2·5 hours, the excess of alcohol was then removed, and the residue was poured into water and extracted with ether. The oil (7·3 g.) obtained from the extract yielded *p*-tolyl β-phenylethyl ketone (1·5 g.), m. p. 69—70°; the residual oil solidified below 0°, but immediately liquefied on warming to the room temperature. The latter was oximated in the usual manner, and the resulting liquid mixture of oximes, when kept in a vacuum, deposited a crystalline oxime, which separated from petrol in colourless needles, m. p. 85—86°, identical with phenyl β-*p*-tolylethyl ketoxime (p. 921).

Ozonolysis. A solution of the mixed acetates in chloroform was treated with ozonised oxygen for several days. A considerable amount of *p*-toluic acid separated. The mixture obtained on evaporation of the chloroform was separated by means of ether and sodium carbonate into acid and neutral portions. The former consisted of impure *p*-toluic acid containing benzoic acid, some of which was isolated by sublimation. The neutral material was boiled with water for 1 hour and with 15% hydrochloric acid for 4 hours, and the product again divided into neutral and acid portions, as before. The small neutral portion, on treatment with aqueous semicarbazide acetate, gave an incompletely solid mixture of semicarbazones, from which, on crystallisation from glacial acetic acid, *p*-tolualdehyde semicarbazone was obtained. The mixed acids were rubbed with about twice their weight of cold water. The insoluble portion proved to be *p*-toluic acid containing benzoic acid. The aqueous lixiviate, on concentration, deposited first mandelic acid and then an impure mixture, from which a pure acid could not be isolated on account of the small amount and its great solubility. It was therefore oxidised with warm 3% hydrogen peroxide and sodium carbonate. On acidification, sparingly soluble acids were precipitated which on crystallisation from dilute acetic acid yielded *p*-toluic acid.

Action of Cinnamaldehyde on Magnesium p-*Chlorophenyl Iodide. Formation of α-Phenyl-γ-*p-*chlorophenylallyl Alcohol and γ-Phenyl-α-*p-*chlorophenylallyl Alcohol.*—The Grignard reagent prepared from magnesium (6 g.), *p*-chloroiodobenzene (60 g.), ether (100 c.c.), and a trace of iodine was treated at the ordinary temperature with a solution of cinnamaldehyde (33 g.) in ether (72·5 c.c.). The mixture was boiled for 30 minutes and then decomposed with ice

and dilute acetic acid. The ethereal extract was washed with sodium hydrogen sulphite solution, sodium hydrogen carbonate, and water. The residue from the ether was a viscous oil (54 g.) which could not be distilled.

The mixed acetates, prepared by boiling the mixture of alcohols for 6 hours with acetic anhydride, were obtained as a straw-coloured, viscous oil, b. p. 225—226°/13 mm. (Found: C, 71·4; H, 5·1. $C_{17}H_{15}O_2Cl$ requires C, 71·2; H, 5·3%).

Action of bromine. A solution of the mixed acetates (7·4 g.) in carbon tetrachloride, after treatment with bromine (4·2 g.), slowly deposited a *bromide* (1·1 g.), which separated from alcohol in prismatic needles, m. p. 193—194° (Found: C, 45·65; H, 3·3. $C_{17}H_{15}O_2ClBr_2$ requires C, 45·7; H, 3·4%). The viscous mass obtained after evaporation of the solvent was dissolved in hot alcohol. On cooling, a second *bromide* (1·05 g.) separated, which crystallised from alcohol in colourless prisms, m. p. 180° (Found: C, 45·8; H, 3·4. $C_{17}H_{15}O_2ClBr_2$ requires C, 45·7; H, 3·4%). The residue (9 g.) was a very viscous gum.

Conversion into ketones. A solution of the mixed acetates (10 g.) in 20% alcoholic potassium hydroxide solution (200 g.) was boiled for 2·5 hours, and the neutral product isolated as an oil (7·7 g.) This was boiled for 24 hours with alcohol (50 c.c.), hydroxylamine hydrochloride (2·4 g.), and sodium acetate (2·9 g.). Extraction with ether in the usual manner gave a residue (7·8 g.), which partly solidified in a vacuum. The solid was washed with and crystallised from ligroin. It separated in colourless, slender needles, m. p. 117—118°, and was identical with a synthesised sample of *phenyl β-p-chlorophenylethyl ketoxime* (p. 919). The mother-liquor, after evaporation of the solvent, was kept in an evacuated desiccator for several days; further crystallisation then ensued. This solid after draining, crystallised from ligroin in colourless prisms, m. p. 111—112°, and was identical with a synthesised specimen of p-*chlorophenyl β-phenylethyl ketoxime* (p. 920). A mixture of about equal parts of the oximes melted at 86—95°.

Ozonolysis. (a) *The mixed acetates.* A solution of the mixed acetates (7·8 g.) in chloroform was treated with ozonised oxygen for 6 days, the solution being filtered from time to time to remove the precipitated *p*-chlorobenzoic acid (2·8 g.; m. p. 225—235° unpurified; m. p. and mixed m. p. 235—236°, after crystallisation from dilute alcohol). The acid products in the chloroform yielded 0·09 g. of *p*-chlorobenzoic acid (m. p. 230—235°), 0·79 g. of crude benzoic acid (0·49 g., m. p. 115—120°; 0·30 g., m. p. 112—115°) and a residue, which was boiled with hydrochloric acid for 3 hours; the small residue obtained on evaporation to dryness was heat

to 100° to remove benzoic acid and then crystallised from water, mandelic acid being obtained. The neutral product from the chloroform (2·4 g.) was boiled with water for 1 hour and then oxidised at 35—45° with sodium chlorate (0·5 g.) and osmium tetroxide (0·05 g.) in the presence of a little sodium carbonate. The neutral portion of the oxidation product, probably unoxidised material, was small and was not further examined. The acid portion was separated by means of water into a sparingly soluble mixture of acids (small quantity), which on crystallisation from chloroform yielded *p*-chlorobenzoic acid, and a mixture of very soluble acids (main portion). The chloroform solution contained benzoic acid (sublimation). The soluble acids yielded mandelic acid, and a second substance which could not be isolated in the pure condition. It was therefore oxidised with warm 6% hydrogen peroxide and sodium carbonate; on acidification, *p*-chlorobenzoic acid and benzoic acid were obtained.

(b) *The mixed alcohols.* This experiment was carried out like the preceding one with results which were substantially identical both qualitatively and quantitatively.

Preparation of Reference Ketones.

Ethyl p-*Chlorobenzylbenzoylacetate*,
$C_6H_5{\cdot}CO{\cdot}CH(CH_2{\cdot}C_6H_4Cl){\cdot}CO_2Et$.—
An alcoholic solution of ethyl sodiobenzoylacetate prepared from sodium (1·44 g.), ethyl alcohol (20 g.), and ethyl benzoylacetate (12 g.) was boiled for 2 hours with a solution of *p*-chlorobenzyl bromide (12·85 g.) in alcohol (30 c.c.). The product was isolated in the usual way as a colourless, viscous oil, b. p. 240°/12 mm., which later solidified and then crystallised from alcohol in needles, m. p. 54—55° (Found: C, 67·9; H, 5·5. $C_{18}H_{17}O_3Cl$ requires C, 68·2; H, 5·4%).

Phenyl β-p-*chlorophenylethyl ketone*, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4Cl$, was obtained by hydrolysing the above ester with dilute sulphuric acid or barium hydroxide. It separated from alcohol in colourless needles, m. p. 58° (Found: C, 73·6; H, 5·6. $C_{15}H_{13}OCl$ requires C, 73·6; H, 5·4%). The *oxime*, prepared in the usual manner, crystallised from ligroin in colourless, slender needles, m. p. 117—118° (Found: C, 69·6, 69·5; H, 5·5, 5·5; N, 5·5, 5·55; Cl, 13·6, 13·75. $C_{15}H_{14}ONCl$ requires C, 69·4; H, 5·4; N, 5·4; Cl, 13·6%).

Ethyl p-*Chlorobenzoylacetate*, $C_6H_4Cl{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$.—A solution of ethyl acetoacetate (26 g.) in alcoholic sodium ethoxide prepared from sodium (4·6 g.) and alcohol (35 g.) was treated below 10° with p-chlorobenzoyl chloride (17·5 g.). The mixture was then stirred for 30 minutes, and treated in the same way with half the amounts

of sodium ethoxide solution and *p*-chlorobenzoyl chloride originally used. Further additions of still smaller quantities were made in like manner and after the use of sodium ethoxide equivalent to 9·2 g. of sodium, and of 35 g. of the chloride, the mixture was kept for 24 hours and then mixed with ether. The crystals obtained were suspended in water (260 c.c.) and shaken at 40—45° for 20 minutes with ammonium chloride (12 g.) and 10% ammonia (40 c.c.). Extraction with ether gave 32 g. of a pale yellow oil, which on distillation yielded a fraction (20 g.), b. p. 175—185°/15 mm. *Ethyl* p-*chlorobenzoylacetate* boils at 181—182°/18 mm., and solidifies to a mass of needles, m. p. 36° (Found: Cl, 15·5. $C_{11}H_{11}O_3Cl$ requires Cl, 15·65%).

Ethyl benzyl-p-*chlorobenzoylacetate*, $C_6H_4Cl·CO·CH(CH_2Ph)·CO_2Et$, was obtained from ethyl *p*-chlorobenzoylacetate and benzyl bromide in an analogous manner to its isomeride. It distilled at 228—233°/14 mm., and solidified to a crystalline mass, which separated from alcohol in clusters of colourless needles, m. p. 65° (Found: C, 67·8; H, 5·5. $C_{18}H_{17}O_3Cl$ requires C, 68·2; H, 5·4%).

p-*Chlorophenyl* β-*phenylethyl ketone*, $C_6H_4Cl·CO·CH_2·CH_2Ph$, was obtained in colourless, glistening plates, m. p. 78° (from alcohol) by hydrolysis of the above ester with barium hydroxide (Found: C, 72·9; H, 5·3. $C_{15}H_{13}OCl$ requires C, 73·6; H, 5·4%). The *oxime* separates from ligroin in small, colourless prisms, m. p. 111—112° (Found: C, 69·4, 69·5; H, 5·5, 5·55. $C_{15}H_{14}ONCl$ requires C, 69·4; H, 5·4%).

Ethyl *p*-toluoylacetate, $C_6H_4Me·CO·CH_2·CO_2Et$, was prepared in a similar manner to the corresponding *p*-chloro-compound from ethyl acetoacetate (27 g.), sodium (9·5 g.), ethyl alcohol (160 c.c.) and *p*-toluoyl chloride (35 g.). It boiled at 172—173°/14 mm. Marguery (*Bull. Soc. chim.*, 1905, **33**, 549) gives b. p. 170°/30 mm (Found: C, 69·7; H, 6·8. Calc.: C, 69·9; H, 6·8%).

Ethyl benzyl-p-*toluoylacetate*, $C_6H_4Me·CO·CH(CH_2Ph)·CO_2Et$, was prepared from sodium (1·15 g.), ethyl alcohol (25 c.c.), and ethyl *p*-toluoylacetate (10·3 g.), and benzyl bromide (8·5 g.) dissolved in alcohol (25 c.c.). It was distilled at 232—233°/11 mm. (Found: C, 77·0; H, 6·7. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%). On hydrolysis with baryta, *p*-tolyl β-phenylethyl ketone, m. p. 70 was obtained (compare Mailhe, *Bull. Soc. chim.*, 1914, **15**, 325). The *oxime* separated from ligroin in colourless, glistening plates, m. p. 101—102° (Found: C, 80·5; H, 7·2. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2%).

Ethyl p-*methylbenzylbenzoylacetate*,

$$C_6H_5·CO·CH(CH_2·C_6H_4Me)·CO_2Et,$$

was obtained as a colourless, fairly mobile oil, b. p. 223—225°/10 mm

from ethyl benzoylacetate and *p*-xylyl bromide (Found: C, 76·4; H, 6·4. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·8%). On hydrolysis with barium hydroxide *phenyl* β-p-*tolylethyl ketone* was isolated as a low-melting, waxy solid. On oximation *phenyl* β-p-*tolylethyl ketoxime*, *m. p.* 85—86°, *colourless needles from ligroin*, was obtained (Found: C, 80·3; H, 7·3. $C_{16}H_{17}ON$ requires C, 80·3; H, 7·2%).

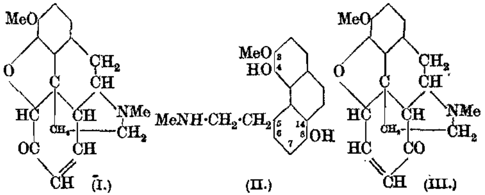
The authors wish to record their thanks to Mr. A. Rumfitt for carrying out the majority of the analyses, and to the Royal Society for a grant with which part of the cost of this investigation has been defrayed.

THE UNIVERSITY, LEEDS. [*Received, February 6th*, 1928.]

CXXII.—*The Constitution of Thebenine.*

By JOHN MASSON GULLAND and CYRIL JOSEPH VIRDEN.

OF the surprising degradations which are found in the chemistry of the morphine alkaloids, perhaps the most remarkable is that in which thebenine (II) is formed (*a*) from thebaine, or (*b*) from codeinone (I), the first product of the hydrolysis of thebaine, or (*c*) from *pseudo*codeinone (III).

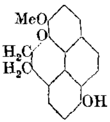


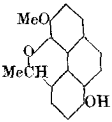
(I.) (II.) (III.)

In the cases (*a*) and (*b*) the conversion readily takes place on heating for a short time with dilute hydrochloric acid (Freund, *Ber.*, 1897, **30**, 1357; 1899, **32**, 168; Knorr, *ibid.*, 1903, **36**, 3074), whereas in (*c*) boiling acetic anhydride is necessary (Knorr and Hörlein, *ibid.*, 1907, **40**, 2037), and the product contains an aromatic phenanthrene nucleus in which the C–C–N group of the parent substance is present in the form of a side chain. The researches of Pschorr and his collaborators (*Ber.*, 1904, **37**, 2780; 1907, **40**, 2001; *Annalen*, 1910, **373**, 51, 75) have demonstrated conclusively the

positions occupied by the methoxyl and hydroxyl groups of thebenine, but the allocation of the side chain to position 5 is based on less definite evidence. It depends on the fact that the product of the exhaustive methylation of thebenine is thebenol, in which the initial vinyl group has reacted further with one of the phenolic hydroxyls. Pschorr (*loc. cit.*) has shown that it is the hydroxyl in position 4, not that in position 8, which is involved in this ring formation, and he assigned to thebenol the formula (IV). In view of the ease of formation and stability of six-membered oxide rings, we prefer to adopt the formula (V) (compare Cahn, J., 1926, 2562). From stereochemical considerations, therefore, and from the fact that thebenol is converted into pyrene when distilled with zinc dust or reduced by hydriodic acid and phosphorus (Freund, *Ber.*, 1897, **30**, 1357; 1910, **43**, 2128), it seems probable that the side chain of thebenine is in position 5, and the experiments which are described in this paper have shown beyond doubt that this is actually the case.

(IV.)



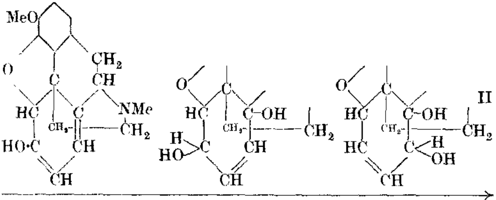


(V.)

Before describing this work in detail, it is necessary to mention two experiments made in order to test the accuracy of a mechanism which has recently been suggested for the thebenine transformation. Schöpf and Borkowsky (*Annalen*, 1927, **458**, 148) explain the formation of thebenine from codeinone by 1 : 4-addition of water (VIa) to the conjugated system produced in an enolic form of codeinone (VI), followed by the codeine–*pseudo*codeine transformation (VIb). The stage (VIa) is the formula which must now be given to the hydroxycodeine * which is obtained by the reduction of 14-hydroxycodeinone (Freund and Speyer, *J. pr. Chem.*, 1916 **94**, 135; Speyer, Selig, and Heil, *Annalen*, 1922, **430**, 1; compar Gulland and Robinson, *Mem. Manchester Phil. Soc.*, 1925, **69** No. 10), and it seemed interesting to test this theory by direc experiment. We have found that 14-hydroxycodeine is quit unaffected by boiling hydrochloric acid (*d* 1·07, the strength use in the preparation of thebenine), and that prolonged heating wit acetic anhydride yields no triacetylthebenine, but a mixture of tw *bases*, one crystalline, the other amorphous, which are still und

* Assuming that this substance is an unsaturated alcohol.

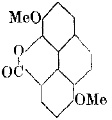
investigation. A consideration of these facts leads us to believe that Schöpf's theory is improbable.

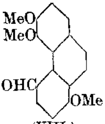


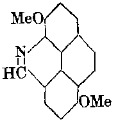
(VI.) (VIa.) (VIb.)

The comparative experiments described in this paper were based *in the first instance on the analogous work which has been carried* out with *apo*morphine and morphothebaine—the methylation of the phenolic hydroxyl groups, the elimination of the nitrogen atom by exhaustive methylation, the conversion of the resulting vinyl group into methoxyl through the stages of carboxylic acid, hydrazide, azide (Curtius, *Ber.*, 1894, **27**, 778), and the comparison of the methoxyphenanthrene thus obtained with a phenanthrene derivative synthesised by Pschorr's method (*Ber.*, 1896, **29**, 496). Pschorr and his collaborators have converted methebenine, the 8-methyl ether of thebenine, into 3 : 4 : 8-trimethoxy-5-vinylphenanthrene, and have oxidised this to 3 : 4 : 8-trimethoxyphenanthrene-5-carboxylic acid. We have experienced no difficulty in preparing these compounds by the same methods, and the *methyl* ester of the acid readily yielded the corresponding *hydrazide*. A solution of this substance in glacial acetic acid on the addition of sodium nitrite deposited the *azide* as an oil which soon crystallised. When the azide was warmed with ethyl alcohol, nitrogen was evolved, but instead of the expected urethane, a crystalline non-nitrogenous substance, $C_{17}H_{12}O_4$, separated in almost theoretical yield. The same compound was obtained when the azide was heated slowly to 65°, or when methyl or amyl nitrite acted on the hydrazide in alcoholic hydrogen chloride solution. Since this substance contains only two methoxyl groups, and dissolves in methyl-alcoholic potash, although scarcely soluble in methyl alcohol, we regard it as the *lactone* of 4-hydroxy-3 : 8-dimethoxyphenanthrene-5-carboxylic acid (VII), and some confirmation of this view is obtained from its formation in the acid hydrolysis of 3 : 4 : 8-trimethoxy-5-cyanophenanthrene (see below), and from the facility with which the same methoxyl is hydrolysed when

methebenol is produced by the crystallisation from acetic acid of the trimethoxyvinylphenanthrene mentioned above.


(VII.)


(VIII.)

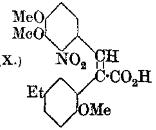

(IX.)

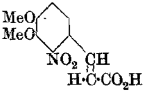
The chief product of the oxidation of 3 : 4 : 8-trimethoxyvinylphenanthrene is a non-acidic substance, $C_{16}H_{16}O_4$, which Pschorr termed "oxymethebenol," but which we have shown by the preparation of an *oxime* and a *semicarbazone* to be 5-*aldehydo*-3 : 4 : 8-*trimethoxyphenanthrene* (VIII). The poor yield (20—30%) of trimethoxyphenanthrenecarboxylic acid led us to try to prepare it from this aldehyde by oxidation, but in this we were unsuccessful in spite of a number of attempts. An indirect method of oxidation was therefore attempted; the oxime of (VIII) yielded 3 : 4 : 8-*trimethoxy-5-cyanophenanthrene* on dehydration by boiling with acetic anhydride and sodium acetate, but this compound appeared to be stable to boiling alcoholic potash, and was converted into (VII) either by boiling with a mixture of hydrochloric and acetic acids, or by hydrolysing the corresponding imino-ester hydrochloride. A by-product of the dehydration of the oxime was a base, $C_{17}H_{13}O_2N$, the properties of which were so reminiscent of those of thebenidine (Vongerichten, *Ber.*, 1901, **34**, 767) that we consider the substance to be 3 : 8-*dimethoxythebenidine* (IX), or the isomeride in which the CH and N are transposed. This transposition is analogous to the rearrangement which takes place when *iso*quinoline is produced by the dehydration of cinnamaldoxime (Bamberger and Goldschmidt, *Ber.*, 1894, **27**, 1954).

The experiments described above indicated that the conversion of methebenine into 3 : 4 : 5 : 8-tetramethoxyphenanthrene was impracticable, and we decided therefore to modify the original scheme. 3 : 4 : 8-Trimethoxy-5-vinylphenanthrene was reduced catalytically to 3 : 4 : 8-*trimethoxy-5-ethylphenanthrene*, which proved to be identical with a specimen prepared synthetically. The materials required for this synthesis were 2-nitroveratraldehyde (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3405; Pisovschi, *ibid.*, 1910, **43**, 2137) and 6-methoxy-3-ethylphenylacetic acid, and the starting point for the preparation of this acid was *p*-ethylanisole, obtained by the reduction of *p*-methoxyacetophenone by Clemmensen's method (*Ber.*, 1914, **47**, 51). This was converted into

6-*methoxy*-3-*ethylbenzaldehyde* by the modification of Gattermann's aldehyde synthesis which has been introduced by Adams and Levine (*J. Amer. Chem. Soc.*, 1923, **45**, 2373; 1924, **46**, 1518), and the aldehyde yielded 6-*methoxy*-3-*ethylphenylacetic acid* in good yield through the intermediate stages of *azlactone* and 6-*methoxy*-3-*ethylphenylpyruvic acid*. The condensation of 2-nitroveratraldehyde with sodium 6-methoxy-3-ethylphenylacetate by heating at 100° with acetic anhydride results in a mixture of trans-α-(6'-*methoxy*-3'-*ethylphenyl*)-2-*nitro*-3 : 4-*dimethoxycinnamic acid* (X) and trans-2-*nitro*-3 : 4-*dimethoxycinnamic acid* (XI). Some derivatives of the second acid (XI) are described in the experimental part of this paper. On reduction with ferrous sulphate and ammonia, the acid (X) yielded trans-α-(6'-*methoxy*-3'-*ethylphenyl*)-2-*amino*-3 : 4-*dimethoxycinnamic acid*, and an aqueous methyl-alcoholic solution of the diazonium sulphate of this amino-acid deposited 3 : 4 : 8-*trimethoxy*-5-*ethylphenanthrene*-9-*carboxylic acid* (XII) on boiling or on addition of copper powder. This acid (XII) lost carbon dioxide when its solution in glacial acetic acid was heated at 230°, and the resulting 3 : 4 : 8-*trimethoxy*-5-*ethylphenanthrene* was identical with the preparation obtained from thebaine.

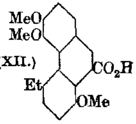
(X.)





(XI.)

(XII.)



EXPERIMENTAL.

The Action of Hydrochloric Acid and Acetic Anhydride on 14-*Hydroxycodeine*.—This base, prepared according to Speyer, Selig, and Heil (*loc. cit.*), was recovered unchanged when ammonia was added to a solution in hydrochloric acid (*d* 1·07) which had been boiled under reflux for 2 hours. It was therefore refluxed with ten times its weight of acetic anhydride for 6 hours; the addition of water to the solution obtained precipitated no non-basic material. Ammonia was added, the precipitate was taken up in chloroform, washed with water, and dried with sodium sulphate, and the solvent was evaporated. When the resinous residue was rubbed with hot alcohol, part dissolved (see below) and part separated in colourless needles, which were collected and recrystallised from ethyl alcohol; m. p. 304° (Found: C, 68·0; H, 5·9%). These figures are in agreement with a number of possibilities, and the substance is still under examination. It is readily

soluble in dilute acetic or hydrochloric acid, and is very sparingly soluble in cold alcohol.

The alcoholic mother-liquor (see above) was evaporated to dryness, and the residue was dissolved in ether, dried, and freed from solvent by distillation. It was a pale yellow oil which dissolved in dilute acetic and hydrochloric acids, and was readily soluble in the usual solvents except ligroin; from this it separated as an oil when a hot solution was cooled. The picrate, hydrochloride, hydriodide, and perchlorate were amorphous.

3 : 4 : 8-*Trimethoxy-5-vinylphenanthrene*.—In preparing the stages intermediate between this substance and thebaine, we have followed closely the details given by Freund and Holthoff (*Ber.*, 1899, **32**, 168) and Pschorr and Massaciu (*Ber.*, 1904, **37**, 2780), but throughout the series of reactions we have been able to improve the yields. Pschorr's method of preparing trimethoxyvinylphenanthrene proved unsatisfactory, and the following process was found more suitable. Dimethylmethebenine methosulphate (m. p. 283—285°; Pschorr and Massaciu give m. p. 268—270°) (12 g.) and *sodium* hydroxide solution (200 c.c. of 20%) were boiled gently under reflux for 12 hours; during the reaction the vinylphenanthrene separated in small, colourless needles (yield, 76%), m. p. 121° (Pschorr gives 122·5° corr.).

3 : 4 : 8-Trimethoxyphenanthrene-5-carboxylic acid (m. p. 236–237°) was obtained as described by Pschorr, Loewen, and Rettberg (*Annalen*, 1910, **373**, 51; m. p. 224—226°) by the oxidation by permanganate of 3 : 4 : 8-trimethoxy-5-vinylphenanthrene in acetone solution. The *methyl* ester separated when a solution of the acid in methyl-alcoholic hydrogen chloride was boiled for 18 hours and allowed to cool. After recrystallisation from methyl alcohol it melted at 149—151°.

The *hydrazide* was prepared by boiling under reflux for 18 hours a mixture of equal weights of the ester, hydrazine hydrate, and ethyl alcohol. It separated on cooling, and crystallised from ethyl alcohol in colourless needles, m. p. 177° (Found: N, 8·4. $C_{18}H_{18}O_4N_2$ requires N, 8·6%).

The *azide* was obtained by the gradual addition of sodium nitrite solution (1·5 c.c. of 5*N*) to a cooled solution of the hydrazide (0·5 g.) in glacial acetic acid (5 c.c.). It separated as an oil which crystallised rapidly, and was collected, washed, and dried on porous tile. The azide decomposed smoothly at 65° when heated slowly (see below), but exploded at 80° if suddenly immersed in a bath at that temperature.

5-*Aldehydo*-3 : 4 : 8-*trimethoxyphenanthrene* (VIII).—The acetone filtrate from the preparation of the trimethoxyphenanthrene

carboxylic acid was evaporated to dryness, and the residual oil, which crystallised on rubbing, was recrystallised first from ethyl alcohol and then from benzene–ligroin. The aldehyde formed *colourless plates*, m. p. 151°, *which were readily soluble in benzene* (Found: C, 72·9; H, 5·5. $C_{18}H_{16}O_4$ reqnires C, 73·0; H, 5·4%).

The *semicarbazone* separated in colourless needles when an aqueous-alcoholic solution of the aldehyde and an excess of semicarbazide hydrochloride and sodium acetate were heated on the water-bath for 2 hours. It was sparingly soluble in the usual solvents, but was recrystallised from nitrobenzene; m. p. 243—246° (decomp.) (Found: N, 11·8. $C_{19}H_{19}O_4N_3$ requires N, 11·6%).

The *oxime* was prepared by boiling under reflux for 2 hours a mixture of the aldehyde, a slight excess of hydroxylamine hydrochloride and potassium acetate, and aqueous alcohol; water precipitated the crude product as an oil which soon crystallised. After drying in a vacuum desiccator, the oxime was crystallised repeatedly from benzene, and dried in a vacuum desiccator, being obtained in dull yellow, lozenge-shaped leaflets, which softened at 110°, became pasty at 140—142°, and were molten at 153° (Found: loss at 100°, 11·5. $C_{18}H_{17}O_4N,\frac{1}{2}C_6H_6$ requires loss, 12·2%. Found in material dried at 100°: N, 4·9. $C_{18}H_{17}O_4N$ requires N, 5·0%). It dissolved readily in warm 2*N*-sodium hydroxide; on cooling, the *sodium* salt separated in cream-coloured leaflets, which redissolved on addition of water.

3 : 4 : 8-*Trimethoxy-5-cyanophenanthrene*.—The oxime described above (4 g.), anhydrous sodium acetate (4 g.), and acetic anhydride (20 c.c.) were boiled under reflux for 6½ hours. After the product had been cooled and mixed with water, the crystalline *nitrile* was collected, washed, pressed on tile (3·5 g.), and crystallised twice from methyl alcohol, forming pale brown needles, m. p. 145—146° (Found: C, 73·8; H, 5·4. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·1%). The nitrile dissolved readily in benzene, forming a solution which exhibited a blue fluorescence, but was sparingly soluble in ether. It crystallised unchanged when a solution in aqueous methyl-alcoholic potash which had been boiled on the water-bath for 5 hours was cooled.

The orange-coloured acid mother-liquor from the preparation of the nitrile contained a small quantity of a base, probably 3 : 8-*dimethoxythebenidine* (IX), which was precipitated by ammonia as a yellow, flocculent mass. This substance was extracted by chloroform, and, after being dried by anhydrous sodium sulphate, it separated as orange-yellow leaflets during the concentration of the solvent. When recrystallised from methyl alcohol, it formed orange leaflets, m. p. 229—230° (Found in material dried at 100°: C, 77·1;

H, 5·1; N, 5·2. $C_{17}H_{13}O_2N$ requires C, 77·6; H, 4·9; N, 5·3%). The properties of this base closely resemble those of thebenidine (Vongerichten, *loc. cit.*). It formed an orange-yellow solution in dilute hydrochloric acid, from which it was precipitated unchanged by alkali, and the colour of the acid solution was almost completely discharged on reduction by tin. The base did not appear to react with nitrous acid. It exhibited pronounced fluorescence in different solvents: in very dilute hydrochloric acid, green; in concentrated sulphuric acid, an intense emerald-green; in chloroform, blue.

The *picrate* separated from a methyl-alcoholic solution of the base and picric acid in wart-like nodules; after recrystallisation from methyl alcohol (bright green fluorescence), it formed orange needles, m. p. 255° (decomp.).

Lactone of 4-*Hydroxy*-3 : 8-*dimethoxyphenanthrene*-5-*carboxylic Acid* (VII).—This substance was obtained from derivatives of 3 : 4 : 8-trimethoxyphenanthrene-5-carboxylic acid in the following ways: (i) A small quantity of the azide was heated gently to 65° and maintained at that temperature until the evolution of gas ceased.

(ii) Methyl nitrite was passed into an ice-cold solution of the hydrazide (2 g.) in alcoholic hydrogen chloride (70 c.c. of 0·3*N*), or alternatively amyl nitrite (0·2 c.c.) was added to an ice-cold solution of the hydrazide (0·1 g.) in alcoholic hydrogen chloride (5 c.c. of 0·5*N*). In either case, on standing overnight, the lactone separated in practically theoretical yield.

(iii) The nitrile (1 g.) was heated on a sand-bath for 6 hours with concentrated hydrochloric acid (15 c.c.) and glacial acetic acid (15 c.c.). The lactone, part of which separated during the reaction, was completely precipitated by the addition of water.

(iv) An ice-cold solution of the nitrile (1 g.) in dry benzene (100 c.c.) and methyl alcohol (2 c.c.) was saturated with dry hydrogen chloride. Next day the light brown needles of the imino-ester hydrochloride (1 g.) were collected, washed with benzene, and dissolved in 50 c.c. of water. When the solution was warmed on the water-bath, the lactone separated in crystalline condition.

The *lactone*, prepared by any of the methods just described, crystallised from glacial acetic acid, in which it was very sparingly soluble when cold, in faintly yellow needles, m. p. 246—247° (Found: C, 72·9; H, 4·3; *M* in camphor by Rast's method, 267. $C_{17}H_{12}O_4$ requires C, 72·9; H, 4·3%; *M*, 280). It was very sparingly soluble in boiling methyl alcohol and insoluble in boiling sodium hydroxide solution, but dissolved readily in hot methyl-alcoholic potash and did not separate on cooling. On addition of water, a clear solution was obtained which immediately began to deposit the unchanged

lactone in an amorphous condition; presumably the potassium salt of the phenolic acid is hydrolysed in aqueous solution. In estimating methoxyl by Zeisel's method, it was necessary to prolong the reaction for a number of hours at 150—160° [Found: OMe, 20·9. $C_{15}H_6O_2(OMe)_2$ requires OMe, 22·1%]. The demethylated substance, presumably the *lactone* of 3 : 4 : 8-trihydroxyphenanthrene-5-carboxylic acid, crystallised from the hydriodic acid, and after being collected and washed with sodium thiosulphate solution, crystallised from ethyl alcohol in colourless needles; it decomposed from 305° onwards, and formed a yellow solution in sodium hydroxide, but was insoluble in bicarbonate solution.

p-*Ethylanisole*.—*p*-Methoxyacetophenone (25 g.) (Gattermann, *Ber.*, 1890, **23**, 1202) was heated on the water-bath for several hours with amalgamated zinc (100 g.) and concentrated hydrochloric acid (Clemmensen, *loc. cit.*), and after being decanted from the excess of zinc the mixture was steam-distilled. Ethylanisole passed over and was taken up in ether, dried with potassium carbonate, and distilled, being obtained as a colourless oil, b. p. 199—200° (Moschner, *Ber.*, 1901, **34**, 1257, gives b. p. 199—200°, and Klages, *ibid.*, 1903, **36**, 3584, b. p. 196—197°). The yield was 40% of that theoretically possible, and there remained a considerable non-volatile residue (compare Steinkopf and Wolfram, *Annalen*, 1923, **430**, 113). Attempts to improve the yield by modifying the conditions were unsuccessful, and the method of Gilman and Hoyle (*J. Amer. Chem. Soc.*, 1922, **44**, 2621) using magnesium, bromoanisole, and ethyl sulphate proved unsatisfactory.

6-*Methoxy-3-ethylbenzaldehyde*.—The aldehydo-group was introduced into *p*-ethylanisole by the method of Adams and Levine (*loc. cit.*). A mixture of *p*-ethylanisole (50 g.), zinc cyanide (95 g.), and dry benzene (350 c.c.) was stirred mechanically in a flask fitted with an inlet for dry hydrogen chloride, an efficient stirrer passing through a mercury seal, and an outlet tube connected through a reflux condenser with a Woulff's bottle containing sulphuric acid. The stirred mixture was saturated with hydrogen chloride (24 hours), aluminium chloride (80 g.) added, and the flask warmed at 50° for 12 hours while the mixture was again saturated with hydrogen chloride. The stirring was then stopped, and next day the upper of the two layers into which the mixture had separated was poured off, and the dark-coloured lower one was hydrolysed by boiling hydrochloric acid (150 c.c. of 3*N*) and submitted to steam distillation. The residual benzene distilled rapidly, and then 6-methoxy-3-ethylbenzaldehyde passed over slowly, and was taken up in ether. The crude oil left by distillation of the ether was converted into the

bisulphite compound, which separated from the hot sodium bisulphite solution on cooling and was then hydrolysed by hot hydrochloric acid. The resulting oil was extracted with ether, washed with water, and dried, and the removal of the ether left the aldehyde (yield 55%), which was converted directly into the azlactone.

6-Methoxy-3-ethylbenzaldehyde is an *oil*, b. p. 261—262°, which was analysed in the form of its *semicarbazone*. The aldehyde (1 g.), semicarbazide hydrochloride (3 g.), and sodium acetate (4 g.) in aqueous alcohol were heated on the water-bath for 2 hours. The semicarbazone, which separated on cooling, crystallised from ethyl alcohol in colourless needles, m. p. 226—227° (Found: N, 19·2. $C_{11}H_{15}O_2N_3$ requires N, 19·0%).

5-Keto-2-phenyl-4-(6′-methoxy-3′-ethylbenzylidene)-4 : 5-dihydro-oxazole, $MeO{\cdot}C_6H_3Et{\cdot}CH{:}C<\begin{matrix}N{:}CPh\\CO\end{matrix}>O$.—This azlactone was obtained by heating together on a water-bath for 30 minutes 6-methoxy-3-ethylbenzaldehyde (10 g.), hippuric acid (12 g.), fused sodium acetate (12 g.), and acetic anhydride (20 c.c.). The yellow solid produced was washed with cold alcohol and repeatedly with boiling water. Further treatment was unnecessary for the next stage, but the azlactone crystallised from acetic acid, ethyl acetate, or ethyl alcohol in bright yellow needles, m. p. 159° (Found: N, 4·5. $C_{19}H_{17}O_3N$ requires N, 4·6%).

6-Methoxy-3-ethylphenylpyruvic acid,

$$MeO{\cdot}C_6H_3Et{\cdot}CH_2{\cdot}CO{\cdot}CO_2H,$$

was prepared from the azlactone (10 g.) by boiling with sodium hydroxide solution (50 c.c. of 10%) for 12 hours. The *sodium* salt of the acid, which separated in colourless plates, m. p. 184°, when the dark liquid was allowed to remain for some hours, was recrystallised from water (Found: loss at 100° after drying in a vacuum desiccator, 3·4. $C_{12}H_{13}O_4Na,\frac{1}{2}H_2O$ requires loss, 3·6%. Found in dried material: Na, 9·2. $C_{12}H_{13}O_4Na$ requires Na, 9·4%). The *acid* was obtained as an oil, which slowly crystallised in needles, by acidifying an aqueous solution of the salt, and the alkaline liquor from which the salt had separated after the hydrolysis of the azlactone yielded a further quantity of the acid when acidified by sulphur dioxide (Haworth, Perkin, and Rankin, J., 1924, **125**, 1686). The total yield was 70% of that theoretically possible.

6-Methoxy-3-ethylphenylpyruvic acid dissolved readily in ethyl alcohol, ether, acetone, or acetic acid, but was somewhat less soluble in methyl alcohol, and crystallised from this solvent in yellow prisms, m. p. 185°, which liquefied on being kept for a short time. Satisfactory analyses of the acid could not be obtained, and it was

therefore analysed in the form of *3-hydroxy-2-(6'-methoxy-3'-ethylbenzyl)quinoxaline*, $MeO{\cdot}C_6H_3Et{\cdot}CH_2{\cdot}C{<}{}^{N\!-\!-\!-\!C_6H_4}_{C(OH){:}N}$, which separated when a hot alcoholic solution of the acid and *o*-phenylenediamine was cooled. This substance crystallised from ethyl alcohol in very small, colourless needles, m. p. 184—185° (Found : N, 9·4. $C_{18}H_{18}O_2N_2$ requires N, 9·5%).

6-*Methoxy*-3-*ethylphenylacetic Acid*, $MeO{\cdot}C_6H_3Et{\cdot}CH_2{\cdot}CO_2H$.—An ice-cold solution of sodium 6-methoxy-3-ethylphenylpyruvate in 2*N*-sodium hydroxide was oxidised by a slight excess of 30% hydrogen peroxide diluted with four volumes of water. Next day the phenylacetic *acid* (85% yield) was precipitated in shining leaflets by dilute sulphuric acid, and was collected, dried, and recrystallised from light petroleum (b. p. 60—80°); it formed colourless leaflets, m. p. 68—69°, which readily dissolved in ethyl alcohol, ether, and benzene (Found in material dried at 100° : C, 67·9; H, 7·6. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). The *sodium* salt was prepared by evaporating to dryness a solution of the acid in the requisite amount of sodium carbonate solution. It was very readily soluble in water.

The Condensation of 2-*Nitroveratraldehyde with* 6-*Methoxy*-3-*ethylphenylacetic Acid.* trans-α-(6'-*Methoxy*-3'-*ethylphenyl*)-2-*nitro*-3 : 4-*dimethoxycinnamic Acid* (X) *and* trans-2-*Nitro*-3 : 4-*dimethoxycinnamic Acid* (XI).—A mixture of sodium 6-methoxy-3-ethylphenylacetate (7 g.), 2-nitroveratraldehyde (14 g.), and acetic anhydride (80 c.c.) was heated under reflux at 100° for 72 hours. Water was then added to destroy the acetic anhydride, and the residual oil was taken up in ether. The ether was repeatedly extracted with sodium carbonate solution, and when the mixed extracts were fractionally precipitated by hydrochloric acid the *acid* (X) separated first; it was recrystallised from ethyl alcohol.

trans-α(6'-*Methoxy*-3'-*ethylphenyl*)-2-*nitro*-3 : 4-*dimethoxycinnamic acid* formed pale lemon-yellow prisms, m. p. 193—194° (Found : C, 62·6; H, 5·5. $C_{20}H_{21}O_7N$ requires C, 62·0; H, 5·4%). The acid dissolved readily in hot dilute ammonia, but on cooling, the *ammonium* salt separated in pale yellow, silky needles.

Both this acid (X) and the acid (XI) (below) have the *trans*-configuration, since on reduction they yield the corresponding amino-acids, and not the carbostyril derivatives (compare Stoermer, *Annalen*, 1915, **409**, 13).

In the fractional precipitation by acid (see above), the partly neutralised solution was decanted from the first oily precipitate when crystals began to separate. The crystals are the acid (XI), and complete precipitation yielded this acid in a comparatively pure

condition; on recrystallisation from ethyl alcohol, trans-*2-nitro-3 : 4-dimethoxycinnamic acid* formed colourless needles, which softened at 217° and melted at 229° (Found: C, 52·5; H, 4·4. $C_{11}H_{11}O_6N$ requires C, 52·2; H, 4·3%). This acid was identical in every way with a specimen prepared by the following method. 2-Nitroveratraldehyde (4 g.), malonic acid (6·3 g.), piperidine (0·5 c.c.), and pyridine (20 c.c.) were heated together on the water-bath for 1 hour, and the mixture was then poured into water and acidified by hydrochloric acid. The precipitated acid was collected, washed, purified by solution in sodium carbonate and reprecipitation, and crystallised from ethyl alcohol, from which it separated in pale yellow needles, m. p. 229° after softening at 217°.

2-*Amino*-3 : 4-*dimethoxycinnamic Acid* (as XI, but with NH_2 instead of NO_2).—A hot ammoniacal solution of the nitro-acid was added to a reducing mixture prepared from the theoretical quantity of ferrous sulphate ($7H_2O$)* and an excess of ammonia. After heating on the water-bath for 20 minutes, the solution was filtered, and the amino-acid precipitated by acetic acid (yield, 65%). This acid crystallised from ethyl alcohol in colourless needles, m. p. 173—178° (decomp.) (Found: N, 6·4. $C_{11}H_{13}O_4N$ requires N, 6·3%). The *hydrochloride* was sparingly soluble, and crystallised from water in colourless leaflets which charred on heating. The *acetyl* derivative was prepared by heating the acid with acetic anhydride on the water-bath for 15 minutes, precipitated with water, and crystallised from ethyl alcohol. It formed colourless needles, m. p. 253° (decomp.), which were soluble in sodium bicarbonate.

7 : 8-*Dimethoxycarbostyril*.—The amino-acid or its acetyl derivative (1 g.) was heated on the water-bath for 15 minutes with acetic anhydride (10 c.c.) and one drop of concentrated sulphuric acid. Water and an excess of sodium bicarbonate were then added; the *carbostyril*, which separated in plates, crystallised from ethyl alcohol in the same form, m. p. 166—168° (Found: N, 6·8. $C_{11}H_{11}O_3N$ requires N, 6·8%). It dissolved in dilute alkali and acid.

trans-α-(6′-*Methoxy*-3′-*ethylphenyl*)-2-*amino*-3 : 4-*dimethoxycinnamic Acid* (as X, but with NH_2 instead of NO_2).—An ammoniacal solution of the corresponding nitro-acid (X) (4·2 g.) was added to a hot reducing mixture prepared by adding ammonia (*d* 0·880; 50 c.c.) in water (35 c.c.) to ferrous sulphate (27·2 g.) in hot water (100 c.c.). After heating on the water-bath for 30 minutes, the

* Experiments on a number of reductions of this type have shown that the use of the theoretical amount of ferrous sulphate is essential. An excess of ferrous hydroxide, if present, passes through the filter, and forms ultimately the insoluble basic acetate.

mixture was filtered and the amino-acid obtained in almost theoretical yield by acidifying the filtrate with acetic acid. It was purified further by solution in hydrochloric acid and precipitation by means of sodium acetate, and after being collected, washed, and dried, was crystallised from benzene; it formed lemon-yellow, flat prisms, m. p. 151—152° (Found: C, 67·2; H, 6·4. $C_{20}H_{23}O_5N$ requires C, 67·2; H, 6·4%), which were very soluble in alcohol but insoluble in light petroleum.

3 : 4 : 8-*Trimethoxy-5-ethylphenanthrene-9-carboxylic Acid* (XII).—The calculated quantity of sodium nitrite solution (freshly standardised; approximately *N*) was added slowly to an ice-cold solution of α-(6′-methoxy-3′-ethylphenyl)-2-amino-3 : 4-dimethoxycinnamic acid (1 g.) in methyl alcohol (16 c.c.) and sulphuric acid (10 c.c. of 2*N*). The clear red solution, diluted with ice-water (30 c.c.), was divided into two parts. (i) On heating, nitrogen was evolved, and the acid (XII) separated as a gum, which crystallised from ethyl alcohol in colourless needles, m. p. 207°. (ii) Copper bronze powder was added to the second part; when the evolution of nitrogen ceased, the solution was made alkaline with sodium carbonate and filtered, and the acid (XII) precipitated by sulphuric acid. The yield in either case was about 35%, and the acid crystallised from benzene in needles, m. p. 207°, which were sparingly soluble in acetic acid (Found: C, 70·1; H, 5·8. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

3 : 4 : 8-*Trimethoxy-5-ethylphenanthrene* was obtained either by the reduction of 3 : 4 : 8-trimethoxy-5-vinylphenanthrene (from thebaine), or by the elimination of the carboxyl group of the acid (XII).

(i) A methyl-alcoholic solution of trimethoxyvinylphenanthrene (1 g.) absorbed a volume of hydrogen equivalent to one molecule when shaken in an atmosphere of the gas in presence of palladinised charcoal (6 g.), prepared as described by Oxford, Perkin, and Robinson (J., 1927, 2389). The filtered solution was evaporated to dryness; the residue crystallised from ethyl alcohol in colourless needles, m. p. 112—113° (Found: C, 77·0; H, 7·0. $C_{19}H_{20}O_3$ requires C, 77·0; H, 6·7%). A cold acetone solution of this substance resisted oxidation by potassium permanganate to a marked extent.

(ii) The acid (XII) (0·6 g.) in glacial acetic acid (30 c.c.) was heated in a sealed tube at 230° for 44 hours. The product was poured into an excess of dilute ammonia and extracted with ether. The extract, after being washed with water and dried with potassium carbonate, was distilled, yielding a dark-coloured oil which was extracted repeatedly with cold methyl alcohol in order to free the product from a black, insoluble residue. The methyl-alcoholic

solution was concentrated (charcoal), and on cooling deposited yellow columns, m. p. 165—166°; the examination of this substance is described below. The methyl-alcoholic mother-liquor was concentrated to a very small volume; 3 : 4 : 8-*trimethoxy*-5-*ethylphenanthrene* then separated, and after recrystallisation from ethyl alcohol (charcoal) melted at 112—113° (Found: C, 77·0; H, 7·1%). There was no depression of the melting point of a mixture of this substance with the preparation described in (i).

The substance, m. p. 165—166°, was recrystallised from ethyl alcohol, and the m. p. remained constant (Found: C, 73·9; H, 5·6%). The properties of this substance were those of a lactone; it dissolved immediately in hot dilute alcoholic sodium hydroxide, and the solution remained clear on dilution with water. Acidification with dilute sulphuric acid precipitated a yellow amorphous acid which became crystalline on standing. It was recrystallised from alcohol, from which it separated in minute prisms, m. p. 155—157° after softening at 140°. This substance dissolved in sodium carbonate, and the melting point of a mixture of it with the original compound, m. p. 165°, was depressed. The amount of material was insufficient for further examination, but it is suggested tentatively that the substance, m. p. 165°, is the *lactone* of 8-hydroxy-3 : 4-dimethoxy-5-ethylphenanthrene-9-carboxylic acid ($C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%).

One of us (C. J. V.) wishes to thank the Goldsmiths' Company for a Senior Studentship and the Department of Scientific and Industrial Research for a grant which have enabled him to take part in this research. The authors acknowledge their indebtedness to the Chemical Society for grants which have defrayed part of the cost of this investigation.

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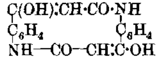
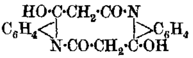
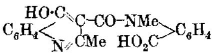
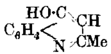
CXXIII.—*The Intermolecular Condensation of Acetylmethylanthranilic Acid by Means of Phosphorus Pentachloride and the Formation of a Complex* iso*Cyanine Dye.*

By ISIDOR MORRIS HEILBRON, SYDNEY LOUIS HOLT, and FRANCIS NOEL KITCHEN.

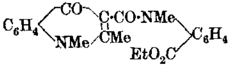
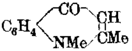
BY the action of phosphoryl chloride upon ethyl acetylanthranilate, Anschütz and Schmidt (*Ber.*, 1902, **35**, 3463) obtained an acid, C[illegible]H[illegible]O[illegible]N[illegible], to which they ascribed the constitution (I) or (II).

(I.)   (II.)

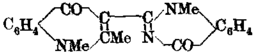
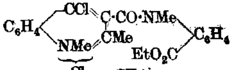
The same compound was incidentally isolated by Heller and
;rundmann (*Ber.*, 1923, **56**, 200) by treatment of benzenesulphonyl-
nthranilic acid with acetic anhydride, followed by hydrolysis of
he sulphonic residue with aqueous sodium hydroxide. These
uthors showed, however, that the constitution must be represented
y (III), because scission of the acid with glacial acetic acid and
ydrochloric acid at 100° gave 4-hydroxyquinaldine (IV).

(III.)   (IV.)

A study has now been made of the complex products obtained by he action of phosphorus pentachloride upon acetylmethylanthr-nilic acid. When the reactants in equimolecular proportion were eated under reflux in presence of acetyl chloride, hydrogen chloride 'as evolved and a substance was gradually deposited which, after reatment with alcohol, finally yielded a product, m. p. 245°, of ormula $C_{22}H_{22}O_4N_2$. After removal of solvent and phosphorus hlorides from the original filtrate, the residual gum was dissolved n alcohol, and a second substance (m. p. 209°), $C_{22}H_{22}O_3N_2Cl_2$, was solated. This compound was the sole product of the reaction 'hen 1½ mols. of phosphorus pentachloride were employed, whereas 'ith only ½ mol. of phosphorus chloride the chlorine-free compound lone was produced. That the latter substance has the structure V), analogous to (III), follows from the isolation of 1 : 2-dimethyl--quinolone (VI) and methylanthranilic acid as products of its ydrolysis by means of concentrated hydrochloric acid.

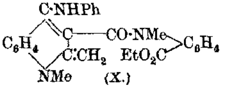
(V.)   (VI.)

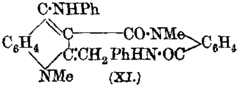
Intermolecular condensation, therefore, must have occurred so is to produce in the first instance the acid chloride (VII; = V with 'OCl instead of CO_2Et), and this view has been confirmed both by he preparation of the free acid and also by the ready formation of *4 : 4'-diketo-1 : 1' : 2'-trimethyl-1' : 4'-dihydro-2(3')-quinolylquin-zoline* (VIII) on treatment of the original reaction product (VII) vith concentrated ammonia.

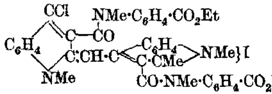
(VIII.) (IX.)

The compound $C_{22}H_{22}O_3N_2Cl_2$, m. p. 209°, proved to be the chloride of a monacid base, the second chlorine atom being non-ionic. When refluxed with alcoholic potash, it was readily converted into the chlorine-free *acid* derived from (VII), a reaction reminiscent of the formation of 4-hydroxypyridine derivatives from the corresponding 4-chloro-compounds (compare Sedgwick and Collie, J., 1895, **67**, 399), and one which indicates formula (IX) as representing its structure. The ready formation of the *anilide* (X) when the ester is heated with aniline in acetic acid solution, and the isolation of 4-hydroxyquinaldine methochloride as a product of hydrolysis are in complete harmony with such a formulation.


(X.)


(XI.)

On the other hand, when the original acid chloride from which (IX) is derived was warmed with an excess of aniline, the *methylene base* (XI) was produced, a reaction paralleled by the production of 4-anilino-1-methyl-2-methylene-1 : 2-dihydroquinoline from 4-chloroquinaldine methiodide (compare O. Fischer, Diepolder, and Wölfel, *J. pr. Chem.*, 1925, **109**, 59).


(XII.)

When 4-*chloro*-3-o-*carbethoxyphenylmethylcarbamyl*-2-*methylquinoline methochloride* (IX) is neutralised with aqueous alkali, the free base is precipitated as a yellow solid. This substance is extraordinarily labile and rapidly passes into a purple, gummy dye, soluble in water to a reddish-purple solution, the colour of which is discharged by strong mineral acids. These reactions, and the fact that the anilino-derivative (X) fails to produce a dye, lead to the conclusion that the dye is a member of the *iso*cyanine group. The dye was isolated and analysed in the form of its *iodide* (XII), its formation being analogous to the preparation of a chloro-*iso*cyanine by O. Fischer, Müller, and Vilsmeier from 4-chloroquinaldine methiodide (*J. pr. Chem.*, 1925, **109**, 69).

The action of phosphorus pentachloride upon 5-bromoacetylmethylanthranilic acid has also been studied. This compound was prepared by converting 5-bromoanthranilic acid into its methyl derivative and acetylating this under the conditions described in the experimental part. Attempts to methylate the corresponding

5-*bromoacetylanthranilic acid were unsuccessful.* The course of the reaction with phosphorus pentachloride is completely analogous to that already described, resulting in the formation of 6-*bromo*-3-p-*bromo*-o-*carbethoxyphenylmethylcarbamyl*-1 : 2-*dimethyl*-4-*quinolone* and 4-*chloro*-6-*bromo*-3-p-*bromo*-o-*carbethoxyphenylmethylcarbamyl*-2-*methylquinoline methochloride*.

EXPERIMENTAL.

3-o-*Carbethoxyphenylmethylcarbamyl*-1 : 2-*dimethyl*-4-*quinolone* (V).—Dry acetylmethylanthranilic acid (42 g.) was suspended in acetyl chloride (250 c.c.) and mixed with phosphorus pentachloride (25 g.; ½ mol.). A vigorous reaction started immediately and after the evolution of hydrogen chloride had slackened the whole was heated under reflux on the water-bath. The cream-coloured solid obtained was washed repeatedly with small quantities of acetyl chloride and finally with dry ether, and dissolved in alcohol; a vigorous reaction then occurred which was completed by refluxing the mixture for ½ hour. The cold solution was diluted with water and the crystals obtained after 12 hours were repeatedly crystallised from aqueous alcohol, from which the *quinolone* separated in colourless needles containing $1H_2O$. The hydrated compound melts at 124°, resolidifies at 200°, and melts again at 240°. The anhydrous compound, which is obtained by boiling the hydrate with dry benzene and separates as a microcrystalline powder, melts at 245°. It is fairly easily soluble in warm alcohol, but insoluble in ether and benzene (yield, 62%) (Found: C, 70·2, 70·0; H, 5·7, 5·8; N, 7·5, 7·5. $C_{22}H_{22}O_4N_2$ requires C, 69·8; H, 5·8; N, 7·4%).

The corresponding *methyl* ester, obtained by decomposing the acid chloride with methyl alcohol, also separates as a hydrate, which partly melts at 115°. The anhydrous compound, obtained by crystallisation of the hydrate from dry acetone–chloroform, forms long, prismatic needles, m. p. 244° (Found: C, 69·0; H, 5·5; N, 7·9. $C_{21}H_{20}O_4N_2$ requires C, 69·2; H, 5·5; N, 7·7%).

3-o-*Carboxyphenylmethylcarbamyl*-1 : 2-*dimethyl*-4-*quinolone*.—The chloride (VII) was warmed with dilute sodium hydroxide solution, and the acid precipitated with hydrochloric acid. Recrystallised from aqueous alcohol, it separated as a hydrate, m. p. 130—131°. The anhydrous acid was obtained, by crystallisation from acetone–chloroform, in colourless prisms, m. p. 247°, soluble in alcohol, insoluble in ether and benzene (Found: C, 68·4, 68·6; H, 5·2, 5·2; N, 8·2. $C_{20}H_{18}O_4N_2$ requires C, 68·6; H, 5·2; N, 8·0%).

The *anilide*, prepared by warming the acid chloride with aniline, crystallised from aqueous alcohol (charcoal) in lustrous plates, m. p. 115° (Found: N, 10·1. $C_{26}H_{23}O_3N_3$ requires N, 9·9%).

4 : 4′-*Diketo*-1 : 1′ : 2′-*trimethyl*-1′ : 4′-*dihydro*-2(3′)-*quinolylqui*
azoline (VIII) was prepared by treating the acid chloride with c
concentrated ammonia; after the vigorous reaction had ceased, t
mixture was diluted with water. The *quinazoline* crystallised fr
alcohol in colourless prisms, m. p. 260° (Found : N, 11·8. $C_{20}H_{17}O_2$
requires N, 12·0%). It is readily soluble in warm dilute hyd
chloric acid and separates unchanged on cooling.

Acid Hydrolysis of 3-o-Carbethoxyphenylmethylcarbamyl-1 : 2-
methyl-4-quinolone.—The quinolone (3 g.) was boiled for 6 ho
under reflux with concentrated hydrochloric acid (10 c.c.); 1 : 2-
methyl-4-quinolone hydrochloride separated on cooling. The fr
base, isolated by means of dilute ammonia, formed colourl
needles, m. p. 175—176° (Found : C, 76·1 ; H, 6·3 ; N, 8·0. Ca
for $C_{11}H_{11}ON$: C, 76·3 ; H, 6·4 ; N, 8·1%).

4 - *Chloro* - 3 - o - *carbethoxyphenylmethylcarbamyl* - 2 - *methylquinol*
Methochloride (IX).—Dry acetylmethylanthranilic acid (15
was suspended in acetyl chloride (150 c.c.) and treated with ph
phorus pentachloride (25 g.; 1½ mols.). When the evolution
hydrogen chloride had almost ceased, the mixture was refluxed
the water-bath until all the solid had dissolved to form a deep r
solution. The thick red gum left after removal of the solvent a
phosphorus chlorides under reduced pressure was warmed w
absolute alcohol, and the resultant red solution mixed with
equal volume of ethyl acetate. The cream-coloured needles whi
separated on standing were repeatedly crystallised from alco
(charcoal), and the *methochloride*, finally crystallised by addition
ethyl acetate, was obtained in colourless needles, m. p. 209° (decom
to a purple mass), readily soluble in alcohol and water, sparing
soluble in ethyl acetate, insoluble in ether and benzene (yield, 50%
The free base was precipitated by aqueous alkali as a yellow sol
which rapidly turned purple and formed a tar. The methochlori
may also be prepared by treating 3-o-carbethoxyphenylmeth
carbamyl-1 : 2-dimethyl-4-quinolone as described above with ph
phorus pentachloride (1 mol.) (yield, 66% of the quinolone employe
(Found : C, 58·6, 58·4 ; H, 5·4, 5·3 ; N, 6·4, 6·5 ; total Cl, 15·
ionised Cl, 7·9. $C_{22}H_{22}O_3N_2Cl_2,H_2O$ requires C, 58·5 ; H, 5·
N, 6·2 ; total Cl, 15·7 ; ionised Cl, 7·9%).

Salts. The *methoperchlorate*, precipitated from an aqueous so
tion of the methochloride by perchloric acid in slight exce
crystallised from alcohol, containing a few drops of perchloric ac
in colourless needles, m. p. 224—225° (decomp. to a purple mas
When heated in a flame, it melted and then decomposed explosive
(Found : N, 6·0. $C_{22}H_{22}O_7N_2Cl_2$ requires N, 5·6%).

The *methiodide*, obtained from potassium iodide and the meth

chloride in aqueous solution, separated from aqueous alcohol in golden-yellow needles, much less soluble in water and alcohol than the corresponding chloride. It became purple-red at 210° and decomposed to a dark red mass at 215° (Found: C, 50·1; H, 4·3. $C_{22}H_{22}O_3N_2ClI$ requires C, 50·4; H, 4·2%).

The *methopicrate* separated from aqueous alcohol, in which it dissolved to a dark red solution, in golden-yellow needles, decomp. 168—169° [Found: N, 13·4.

$$C_{22}H_{22}O_3N_2Cl(O{\cdot}C_6H_2O_6N_3),C_6H_2(NO_2)_3{\cdot}OH$$

requires N, 13·2%].

*4-Chloro-3-*o*-carbomethoxyphenylmethylcarbamyl-2-methylquinoline methochloride*, prepared by treating the gummy acid chloride with methyl alcohol and precipitated from the resulting red solution by ethyl acetate, crystallised from ethyl alcohol, on addition of ethyl acetate, in white needles. These began to turn purple at 145° and melted to a purple mass at 189—190° (Found: C, 57·7; H, 5·3; N, 6·8. $C_{21}H_{20}O_3N_2Cl_2,H_2O$ requires C, 57·7; H, 5·0; N, 6·4%). The *methiodide* formed golden-yellow needles, m. p. 214° (decomp.) (Found: N, 5·7. $C_{21}H_{20}O_3N_2ClI$ requires N, 5·5%).

*4-Anilino-3-*o*-carbethoxyphenylmethylcarbamyl-1-methyl-2-methylene-1 : 2-dihydroquinoline* (X).—The red solution obtained by refluxing 4-chloro-3-*o*-carbethoxyphenylmethylcarbamyl-2-methylquinoline methochloride (2 g.) and aniline (2 g.) in glacial acetic acid (5 c.c.) for 1 hour was diluted with water, extracted with ether to remove acetanilide, and rendered alkaline. The precipitated *methylene base*, removed and dried in ether, crystallised from alcohol (charcoal), on slight dilution with water, in orange prisms, m. p. 191—192°; it dissolved readily in mineral acids to give yellow solutions (Found: C, 74·5; H, 6·1; N, 9·3. $C_{28}H_{27}O_3N_3$ requires C, 74·2; H, 6·0; N, 9·3%).

The corresponding *4-piperidino-methylene base* was obtained in a similar manner by refluxing an alcoholic solution of the ethyl ester with piperidine. It separated from benzene–light petroleum in yellow needles, m. p. 260°, readily soluble in dilute acids and the usual organic solvents with the exception of light petroleum (Found: C, 73·0; H, 6·9; N, 9·8. $C_{27}H_{31}O_3N_3$ requires C, 72·8; H, 7·0; N, 9·4%).

*4-Anilino-3-*o*-anilinophenylmethylcarbamyl-1-methyl-2-methylene-1 : 2-dihydroquinoline* was obtained by refluxing the acid chloride reaction product with aniline; the whole set to a brittle mass, which was extracted with alcohol. The yellow powder precipitated on dilution of the alcoholic solution with dilute hydrochloric acid was repeatedly dissolved in alcohol and precipitated with water. Although readily soluble in alcohol, benzene, and acetone, giving

deep red solutions showing a brilliant green fluorescence, this compound could not be obtained in a crystalline form. It melted indefinitely at about 165° with previous softening (Found: N, 11·6. $C_{32}H_{28}O_2N_4$ requires N, 11·2%).

Acid Hydrolysis of 4-*Chloro*-3-o-*carbethoxyphenylmethylcarbamyl*-2-*methylquinoline Methochloride*.—The ester (5 g.) was gently boiled for 6 hours under reflux with concentrated hydrochloric acid (150 c.c.), and the cooled solution was almost neutralised with alkali and extracted with ether to remove methylanthranilic acid. The aqueous portion was concentrated under reduced pressure; 4-hydroxyquinaldine methochloride, which separated slowly, after several crystallisations from alcohol–ether, was obtained in colourless needles, m. p. 217° (Found: C, 58·2; H, 6·3; N, 6·5. Calc. for $C_{11}H_{12}ONCl,H_2O$: C, 58·2; H, 6·2; N, 6·2%).

4′-*Chloro*-3 : 3′-*di*(o-*carbethoxyphenylmethylcarbamyl*)-1 : 2 : 1′-*trimethyl*iso*cyanine Iodide* (XII).—A solution of 4-chloro-3-o-carbethoxyphenylmethylcarbamyl-2-methylquinoline methochloride (2 g.) in hot absolute alcohol, when treated with 10 c.c. of dilute ammonia (equivalent to 0·24 c.c. of NH_3 *d* 0·88), became reddish-purple; it was boiled for ½ hour and then treated with a slight excess of concentrated potassium iodide solution. The *iodide* slowly separated from the cold solution in tiny, brownish-olive needles having a bronze reflex. On heating, the salt darkened at 200° and decomposed to a black mass at 203°. It was somewhat sparingly soluble in water and alcohol, giving intense purple solutions the colour of which was discharged on addition of excess of mineral acid. The dye showed two well-defined bands with heads at 574 μμ and 325 μμ (Found: C, 59·5; H, 4·6; N, 6·5. $C_{44}H_{42}O_6N_4ClI$ requires C, 59·7; H, 4·8; N, 6·3%). The *perchlorate* formed a heliotrope powder soluble in alcohol and benzene to purple solutions. The *picrate*, precipitated from an alcoholic solution of the iodide by means of sodium picrate, separated in wine-coloured needles with a metallic reflex, containing two molecules of picric acid; it is practically insoluble in water and sparingly soluble in alcohol (Found: N, 11·4. $C_{56}H_{47}O_{10}N_{10}Cl$ requires N, 11·5%).

5-*Bromomethylanthranilic Acid*.—Methylanthranilic acid (22·5 g.) was dissolved in chloroform, and bromine (24 g.) slowly run in. The solid obtained, after being washed with cold chloroform, crystallised from dilute alcohol in cream-coloured needles, m. p. 185—186° (yield, 73%). Mixed with 5-*bromomethylanthranilic acid* prepared by Wheeler and Oates's method (*J. Amer. Chem. Soc.*, 1910, **32**, 770), it showed no depression of m. p. (Found: N, 6·4. $C_8H_8O_2NBr$ requires N, 6·1%).

5-*Bromomethylacetylanthranilic Acid*.—Great difficulty was ex-

perienced in acetylating 5-bromomethylanthranilic acid. By the use of acetic anhydride alone, a high-melting compound (above 300°) was obtained which was not further examined. The method finally adopted consisted in refluxing the acid (12 g.) with a mixture of acetic anhydride (70 c.c.), glacial acetic acid (5 c.c.), water (10 c.c.). and a trace of *d*-camphorsulphonic acid. The solution was poured into water, and the solid recrystallised from dilnte alcohol. *5-Bromomethylacetylanthranilic acid* forms colourless prisms, m. p. 204° (yield, 70%) (Found: C, 44·4; H, 3·6. $C_{10}H_{10}O_3NBr$ requires C, 44·1; H, 3·7%).

6-Bromo-3-p-bromo-o-carbethoxyphenylmethylcarbamyl-1:2-dimethyl-4-quinolone.—The above acid (5 g.) was snspended in acetyl chloride (50 c.c.) and treated with phosphorus pentachloride (2 g.; ½ mol.). No reaction occurred in the cold, but on heating on the water-bath under reflux the original solid material dissolved to a yellow solution, from which a yellow solid gradually separated. This was worked up in a precisely similar manner to that detailed in the case of the parent quinolone. The *ester*, crystallised from alcohol and then from acetone, was obtained as a hydrate, m. p. 123°. The anhydrous compound, which forms colourless crystals, m. p. 212°, was obtained by dissolving the hydrated product in boiling benzene and allowing the solution to crystallise after the addition of light petroleum (Found: C, 49·2; H, 3·9; N, 5·6. $C_{22}H_{20}O_4N_2Br_2$ requires C, 49·3; H, 3·7; N, 5·2%).

4-Chloro-6-bromo-3-p-bromo-o-carbethoxyphenylmethylcarbamyl-2-methylquinoline methochloride was prepared by heating 5-bromomethylacetylanthranilic acid with phosphorus pentachloride (1½ mols.) in acetyl chloride solution as described under the preparation of (IX). The residual gum was decomposed with alcohol, and the *methochloride* precipitated from the resultant deep red solution by addition of ether. The product crystallised from alcohol–ether in colourless needles, m. p. 194°. It exhibited the same properties as the parent compound and readily passed into the *iso*cyanine dye on treatment with alkali (Found: C, 43·3; H, 4·0; N, 5·0. $C_{22}H_{22}O_3N_2Cl_2Br_2,H_2O$ requires C, 43·3; H, 3·6; N, 4·6%).

We desire to express our thanks to the Advisory Council of the Department of Scientific and Industrial Research and to the Directors of the United Alkali Company for grants which have enabled this work to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, January 24th, 1928.*]

CXXIV.—*The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part IV. The Establishment of the Structure of Selachyl and Batyl Alcohols as Monoglyceryl Ethers.*

By Isidor Morris Heilbron and William Morgan Owens.

The fact that selachyl and batyl alcohols, either together or associated with squalene, are common constituents of the unsaponifiable matter of many shark- and ray-liver oils was first demonstrated by Tsujimoto and Toyama (*Chem. Umschau*, 1922, **29**, 27, 35, 43), who showed that batyl alcohol is the saturated dihydro-derivative of selachyl alcohol, is dihydric, and has a molecular formula corresponding to either $C_{20}H_{42}O_3$ or $C_{21}H_{44}O_3$.

In a further important contribution to the subject, Toyama (*Chem. Umschau*, 1924, **31**, 61, 153) concluded that the latter formula was in better agreement with the analytical results of a carefully purified specimen of the alcohol (m. p. 70·4—71°) regenerated from its diacetyl derivative. The discovery of another saturated alcohol of formula $C_{19}H_{40}O_3$, to which the name chimyl alcohol (m. p 60·5—61·5°) was given, was also reported, and attention wa directed to an interesting and possibly important relationshi between the alcohols present in sperm oil (Tsujimoto, *Chem Umschau*, 1925, **32**, 127) and those under discussion. For instanc a compound of the composition of batyl alcohol would result fro octadecyl alcohol in the following manner :

$$C_{18}H_{38}O + C_3H_8O_3 - H_2O = C_{21}H_{44}O_3.$$

In a similar way, selachyl alcohol would be related to ole alcohol, and chimyl alcohol to cetyl alcohol.

It is curious that, in spite of the above far-sighted implication, t structures of these alcohols, to which so much attention has recent been directed in connexion with work on vitamin-*A* (Drummor Channon, and Coward, *Biochem. J.*, 1925, **19**, 1047), have not up the present been worked out. The only definite observatic hitherto made regarding their constitutions deal with selac alcohol, the acetate of which Toyama (*loc. cit.*) found yielded non acid on oxidation with potassium permanganate, and its dry dist ation led to the isolation of a fraction identical with oleyl alco These results permit of the formula of selachyl acetate being expres as $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot C_{11}H_{21}O(O\cdot CO\cdot CH_3)_2$. The present co munication deals with the structure of batyl alcohol which we isola from the liver oil of *Centrophorus granulosus* (compare Chapm

Analyst, 1927, **52**, 622), in which it occurs in small quantity associated with selachyl alcohol and squalene. Our first inquiry was directed towards elucidation of the nature of the groups associated with the third oxygen atom. According to Weidemann (*Biochem. J.*, 1926, 20, 685), this is present as a methoxy-group, a result deduced apparently from a Zeisel determination and calculation of the precipitated silver iodide as methoxyl. It seemed to us, however, from *a priori* reasoning extremely unlikely that such a grouping would exist in a substance obviously related to the natural fats, and, as detailed in the experimental part, repetition of this work speedily convinced us that, although the molecule certainly contained an ether oxygen atom, it was not present as methoxyl. On the other hand, we have been able definitely to establish the formation of octadecyl iodide by the action of hydriodic acid on batyl alcohol, and have verified this by conversion of the iodide into octadecyl alcohol, which was identified both by a mixed melting-point determination with an authentic specimen, and also through the preparation of its characteristic phenylurethane. Unfortunately, owing to the small amount of material at our disposal, we have been unable to detect the presence of *iso*propyl iodide, but there can be absolutely no doubt that batyl alcohol is in effect a monoglyceryl ether of octadecyl alcohol to which one or other of the following formulæ may be ascribed :

(I.) $C_{18}H_{37}\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ $C_{18}H_{37}\cdot O\cdot CH(CH_2\cdot OH)_2$ (II.)

From the ease of formation of the diacetyl derivative and the phenylurethane, which we have now prepared and which, owing to its definite crystalline character and sharp melting point, is an excellent derivative for the identification of the alcohol, we rather favour formula (II).

We are at present engaged in attempted syntheses of both types of compound, and also other derivatives. It follows from the above that formulæ can also be ascribed to both selachyl alcohol and chimyl alcohol, and that the connexion referred to above on which Toyama (*loc. cit.*) focussed attention is real in all respects.

The occurrence of these glyceryl ethers in nature, forming as they do a link between the fats and waxes, is a matter of much biological interest. The following expression clearly indicates the three types and their inter-relation :

Fat	$(R\cdot CO\cdot O\cdot)_3C_3H_5$
Wax	$R\cdot CO\cdot OR'$
Ethers	$R'O\cdot C_3H_5(OH)_2$.

EXPERIMENTAL.

The residual liver oil (2500 g.) obtained from *Centrophorus granulosus*, after removal of the bulk of the squalene by distillation at 3 mm. (compare Heilbron, Kamm, and Owens, J., 1926, 1638), was saponified by refluxing with boiling alcoholic sodium hydroxide (90 g. in 2500 c.c. of industrial alcohol) for 5 hours. The alcohol was removed as far as possible by evaporation in a vacuum and the semi-solid residue was mixed with silver sand and thoroughly dried by stirring at 70°, after which it was thinned out with glass beads and extracted with hot acetone in a large Soxhlet extractor until the runnings were colourless. After removal of the acetone, the solid material was extracted with ether, the solution repeatedly washed with water to remove soap and dried over sodium sulphate, and the ether distilled. A solution of the residue in pentane, when vigorously stirred at −10°, deposited a very fine crystalline solid, which was collected on kieselguhr. After all oily matter had been washed away with ice-cold pentane, the material was dissolved out of the kieselguhr with dry ether. The crude solid obtained after removal of the ether gave, after one crystallisation from alcohol, lustrous plates m. p. 60—63° (40 g.). This method of working up the batyl alcoho is preferred to the one described by Tsujimoto and Toyama (*Chem Umschau*, 1922, **29**, 28), whereby the alcohol is obtained by freezing an acetone solution of the unsaponifiable matter. The solid material prepared as above failed to show the presence o cholesterol when tested with digitonin.

The pure alcohol was obtained, after repeated fractional crystallisation from alcohol, in colourless laminæ, m. p. 69—70° (27 g. (Found: C, 72·8, 72·8, 72·9; H, 12·8, 12·6, 12·9. Calc. fo $C_{21}H_{44}O_3$: C, 73·2; H, 12·9%).

The *phenylurethane* was prepared by heating the alcohol (1 g to boiling with an excess of phenylcarbimide (3 c.c.) and then reflux ing the mixture with dry benzene (15 c.c.) for 3 hours. After th solvent and the excess of phenylcarbimide had been removed a 15 mm., the residue was extracted with cold dry ether, the solutio filtered, and the ether evaporated. The urethane was firs crystallised three times from benzene and finally from either alcoh or aqueous acetone, from which it separated in tufts of lon irregular needles, m. p. 98° (Found: C, 71·9; H, 9·3; N, 5· $C_{35}H_{54}O_5N_2$ requires C, 72·2; H, 9·3; N, 4·8%).

Batyl p-*nitrobenzoate*. The alcohol (3·4 g.), dissolved in co pyridine (25 c.c.), was slowly treated with *p*-nitrobenzoyl chlori (3·6 g.). Some heat was evolved and the whole set to a dark re crystalline mass, which was warmed for 1 hour at 50°. Aft

12 hours, the reaction mixture was poured into ice-cold dilute hydrochloric acid, and the precipitated solid dissolved in ether. The ethereal solution was washed with dilute sodium carbonate solution and with water and dried over sodium sulphate, and the ether allowed to evaporate. By repeated extraction of the resinous product with dry methyl alcohol, the p-*nitrobenzoate* was obtained in pale yellow, fern-like clusters, m. p. 53—54°, which darkened somewhat on exposure to sunlight [Found : C, 63·2, 63·2; H, 7·9, 8·1; N, 4·3. $C_{21}H_{42}O(O{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2)_2,2CH_3{\cdot}OH$ requires C, 62·9; H, 8·2; N, 4·0%].

Examination of Batyl Alcohol for the Presence of Alkyloxy-radicals.—A qualitative experiment by the Pregl–Zeisel method gave a precipitate of silver iodide, showing the presence of an ether oxygen atom in the molecule (Weidemann, *loc. cit.*). That the ether, however, was not easily ruptured was evidenced by the fact that the decomposition was not complete in the ordinary time (20 minutes) and that variable values, calculated as –OMe, were obtained: 20 minutes, 6·22, 8·8; 25 minutes, 7·4; 30 minutes, 8·2%.

Test for methoxyl. The testing solution consisted of aqueous trimethylamine (24 drops of 33%) in 2 c.c. of absolute alcohol (compare Willstätter and Utzenger, *Annalen*, 1911, **382**, 148). Batyl alcohol (15 mg.) was treated with hydriodic acid (3·2 c.c., *d* 1·7) for 30 minutes, but no precipitate appeared in the absorbing liquid. On removal of the alcohol under reduced pressure, a small amount of an oil having a garlic-like odour (possibly allyl iodide) was obtained. As vanillin (8 mg.) on similar treatment gave in two consecutive experiments a copious crystalline precipitate of tetramethylammonium iodide, it can be inferred that no methoxyl group is present in batyl alcohol, and this probably also applies to ethoxyl and propoxyl.

Formation of Octadecyl Iodide.—Batyl alcohol (10 g.) was refluxed with hydriodic acid (30 c.c., *d* 1·7) for 1 hour. The reaction mixture was taken up in ether, and the solution washed successively with dilute aqueous sodium bisulphite, sodium carbonate solution, and water. After drying, the ether was removed and the residual pale yellow oil poured into alcohol, from which needles immediately separated. These were thrice recrystallised from alcohol–acetone, from which the octadecyl iodide separated in lustrous needles, m. p. 33°. Gascard gives 33·5° (*Ann. Chim.*, 1921, **15**, 340) [Found : (micro) C, 56·8; H, 9·8; I, 32·3, 34·2; *M*, 415. Calc. for $C_{18}H_{37}I$: C, 56·8; H, 9·7; I, 33·5%; *M*, 380].

Preparation of Octadecane.—The iodide (2 g.) was dissolved in a mixture of acetic acid (20 c.c.), previously saturated with hydrogen chloride, and ether (10 c.c.). Zinc dust (5 g.) was then added during

½ hour. The reaction, which was at first rapid but gradually abated, was completed by warming on the water-bath and allowing the ether to evaporate. The mixture was boiled for a further ½ hour, the solvent was then removed by distillation under diminished pressure, and the residue was poured into water and extracted with ether. The ethereal solution was washed with dilute aqueous sodium carbonate and with water, dried, and evaporated. The residual low-melting solid still contained a small amount of halogen, which was removed by repeating the above process. The crude hydrocarbon was repeatedly crystallised from ether–methyl alcohol, from which it separated in long, colourless needles, m. p. 28—29° (Gascard, *loc. cit.*, gives 27—28°), very readily soluble in ether, hexane, and acetone [Found : (micro) C, 84·7 ; H, 15·0 ; *M*, 274, 264. Calc. for $C_{18}H_{38}$: C, 85·0 ; H, 15·0% ; *M*, 254]. The reduction of the iodide to octadecane can also be carried out by Stephen's method (J., 1914, **105**, 1050) with zinc in an alcohol–acetic acid solution.

Octadecyl Methyl Ether.—The iodide (2 g.) was refluxed for 2 hours with an excess of alcoholic sodium methoxide (2 g. of sodium in 20 c.c. of methyl alcohol) and the reaction mixture was diluted with water and extracted with ether. The extract was thoroughly washed with water and dried over anhydrous sodium sulphate. *Octadecyl methyl ether* crystallised from ether–methyl alcohol in very fine laminæ, m. p. 30—31° [Found : (micro) C, 80·3 ; H, 13·9. $C_{19}H_{40}O$ requires C, 80·3 ; H, 14·1%].

Octadecyl Alcohol.—The iodide (4 g.) together with silver acetate (4 g.) was refluxed with absolute alcohol (100 c.c.) for 6 hours. The supernatant liquid was decanted, the residue well washed with acetone, and the combined liquids were worked up as described in the preparation of octadecane. The acetate, obtained as a colourless, low-melting solid, was without further purification heated under reflux with methyl-alcoholic potassium hydroxide. The hydrolysed product was diluted with water and extracted with ether and, after drying and removal of solvent, the crude octadecyl alcohol was crystallised from acetone and finally from 92% alcohol. It formed colourless crystals, m. p. 57—58°, alone or mixed with an authentic specimen. The alcohol was also characterised by the preparation of its phenylurethane, which crystallised from alcohol in feathery needles, m. p. 77—78° (André and Francis give 79—80° ; *Compt. rend.*, 1926, **183**, 663) [Found : (micro) C, 76·9 ; H, 11·2 ; N, 3·7. Calc. for $C_{25}H_{43}O_2N$: C, 77·1 ; H, 11·1 ; N, 3·6%].

Detection of Selachyl Alcohol.—The presence of this alcohol in the liver oil of *Centrophorus granulosus* has already been detected by Chapman (*loc. cit.*), whose statement regarding the impossibility of separating it entirely from squalene (spinacene) we fully confirm

Chapman hydrogenated it to batyl alcohol by means of platinum-black, and we have obtained the same result using a nickel catalyst at 150°, and working on the residues obtained after removal of as much solid batyl alcohol as possible.

In conclusion, we desire to thank the Food Investigation Board for a grant which has enabled this research to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, February 13th*, 1928.]

CXXV.—*The System Sodium–Tin.*

By WILLIAM HUME-ROTHERY.

IN connexion with the problem of intermetallic compounds, the alloys of the alkali and alkaline-earth metals are of particular interest, since in these one metal at least is of well-defined chemical nature. The present author (*J. Inst. Metals*, 1926, **35**, 295) has already investigated the alloys of tin with calcium and magnesium, and the work is now extended to the alloys with sodium.

According to Mathewson (*Z. anorg. Chem.*, 1905, **46**, 94), the system sodium–tin is very complex, and contains the compounds Na_4Sn, Na_2Sn, Na_4Sn_3, NaSn, and $NaSn_2$. Of these, the last three were regarded as undergoing polymorphic transformations, but the evidence on this point was inconclusive, since only cooling curves were studied. No systematic examination by means of annealing experiments and microscopical investigation was made.

The only other detailed work on this system appears to be that of Kremann and Gmachl-Pammer (*Inter. Z. Metal.*, 1920, **12**, 257), who investigated the electromotive behaviour of these alloys in solutions of sodium iodide in pyridine, and of the tin-rich alloys in aqueous solutions. They confirmed the existence of the compounds Na_4Sn, Na_2Sn, NaSn, and $NaSn_2$, but not of Na_4Sn_3.

EXPERIMENTAL.

Materials.—The sodium used in the present work was pure electrolytic metal. No other metals could be detected by the ordinary methods of analysis, and, apart from superficial oxidation and occasional inclusions of hydroxide, the material appeared satisfactorily pure. It froze at a constant temperature. The tin was the " Chempur " tin of Messrs. Capper Pass and Co., and was accepted as being of sufficient purity.

Procedure.—The reactivity of these alloys necessitated the use of closed vessels for all the cooling-curve experiments, which were carried out in an atmosphere of nitrogen. The alloys were melted

in hard glass tubes of 1—1·3″ diameter, and for the sodium-rich alloys Pyrex glass was the most suitable; no appreciable error is likely to have resulted from action between the alloy and the glass, since the two could always be separated cleanly, and, except for a very thin dark film on the inside, the tubes appeared unaffected. These tubes were then placed inside a large, hard-glass tube about 12—14″ long and 1·5″ in diameter, fitted with a rubber bung through which passed glass tubes carrying the stirrer, the thermocouple, and a tube for the passage of a slow current of nitrogen. The general arrangement was similar to that used by the author for the calcium alloys (*loc. cit.*) but on a rather smaller scale. The thermocouples were of alumel-chromel (No. 26 S.W.G.) and were standardised against the melting points of pure aluminium, zinc, lead, and tin. The thermocouple sheath was made by drawing out a hard-glass tube into a thin capillary just wide enough to contain the wires: for some of the tin-rich alloys, a thin silica sheath coated with alundum cement was used. The thermoelectric force was measured on a Carpenter–Stansfield potentiometer.

For the cooling-curve experiments two types of furnace were used—a well-lagged electric crucible furnace, and a large gas-fired furnace with a damper in the flue to stop the draught during cooling. These gave rates of cooling of about 5° and 10° per minute at 400°, and for convenience these will be referred to as "slow" and "normal" cooling respectively. Heating and cooling curves at slower rates were also taken in special cases.

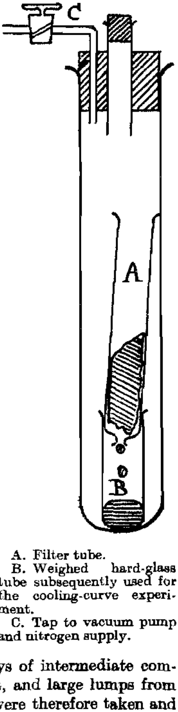
The weights of alloys used in the cooling-curve experiments varied from about 120 g. at the tin end of the diagram to 35 or 40 g. for the sodium-rich alloys. In all cases, thorough stirring was necessary during melting, since there was a great tendency for the sodium to float on the top.

As will be shown later, it was necessary to prepare chill castings of many alloys in order to obtain samples with a very fine structure suitable for annealing experiments. Alloys containing not more than 8% of sodium were melted in an atmosphere of nitrogen, and were then cast in heavy copper moulds bored with holes ¼″ and ⅜″ diameter respectively, so as to give ingots of these diameters and about 4″ long. The large mass and high thermal conductivity of the copper gave a very rapid cooling, and it was largely owing to the very fine structure obtained in this way that the annealing experiments were successful. For the sodium-rich alloys the whole of the casting operation had to be carried out in a closed vessel, and for this purpose an apparatus was devised consisting of a hard-glass tube about 15″ long and 1·4″ in diameter, closed at one end and fitted with a wide side-tube about 6″ from the bottom. In this

side-tube was placed a copper mould made from a 1″ circular bar of pure copper so as to give a square ingot 3″ × ¼″ × ¼″. The alloy was melted in a narrower tube provided with a spout, and of a length such that the spout was situated immediately over the opening of the mould, so that, when the alloy was molten, a casting could be made by carefully tipping the whole apparatus to one side. In this way it was possible to prepare chill castings of sodium-rich alloys from a temperature of about 500°. It is hoped to publish elsewhere further details of this apparatus.

FIG. 1.

Apparatus for obtaining sodium free from oxide for accurate weighing.



A. Filter tube.
B. Weighed hard-glass tube subsequently used for the cooling-curve experiment.
C. Tap to vacuum pump and nitrogen supply.

For microscopical examination the alloys were mounted in fusible metal, and in all except the tin-rich alloys, the grinding, polishing, and photography had to be carried out under oil.

The arrangements for the annealing and quenching experiments were the same as those used by the author and S. W. Rowell (*J. Inst. Metals*, 1927, **38**, 137).

Analytical Methods.—The difference between the atomic weights of sodium and tin, and the steepness of many of the lines in the equilibrium diagram made the accurate analysis of the alloys a matter of great importance, a difference of 0·1% of sodium sometimes corresponding to as much as 10° in the freezing-point curve. The extreme reactivity of the alloys made it essential to determine both constituents, in order to avoid any errors introduced by slight oxidation during weighing, and this has been done in the case of all alloys containing more than 0·5% of sodium, the tin being weighed as dioxide, and the sodium as sulphate.

For the tin-rich alloys, a complete vertical strip of the cooling curve ingot was cut for the analysis, to avoid the effects of any slight segregation. The alloys of intermediate composition were too brittle for this treatment, and large lumps from the top, bottom, and middle of the ingot were therefore taken and

ground to powder under benzene. A suitable amount of the powder was then added to water, and the small amount of benzene boiled off. This was satisfactory for alloys containing up to 35% of sodium, but beyond this point increasing amounts of the compound Na_4Sn are present, and as this reacts explosively with water, it was necessary to allow the powder to oxidise in a porcelain dish before adding water.

In alloys containing more than 44% of sodium, some of this element is in the free state, and the mass cannot be ground to powder; these alloys are, in fact, so dangerous to handle that it was thought better to adopt special methods to avoid oxidation during the melting

TABLE I.

Cooling curve experiments for the determination of the liquidus.

Tin-rich Alloys.

No. of alloy.	Sodium. % by weight.	Sodium. Atomic %.	Arrests on cooling curve. Primary.	Later arrests.			
A1	0	0	232°				
A2	0·073	0·38	231				218°
A3	0·20	1·02	230				221
A4	0·37	1·88	225				220
A5	0·62	3·12	223				220
A6	0·82	4·09	221				
B1	0·99	4·91	224				220
B2	1·18	5·81	232			225°	221
B3	1·24	6·09	238			225	221
B4	1·61	7·79	248			226	220
B5	1·72	8·28	253		227°	225	221
B6	1·80	8·63	254		227	225	221
B7	2·15	10·19	266		228	226	221
B8	2·10	9·97	267		226	225	221
B9	2·29	10·79	268		228	225	221
B10	2·34	11·01	269		228	225	221
B11	2·77	12·82	278		227	224	219
B12	3·03	13·89	289		228	226	221
B13	3·12	14·25	289	286°	229	225	221
B14	3·53	15·91	293	283	231	225	220
B15	3·78	16·85	297	290	229	225	221
C2	4·47	19·45	308	289	228	226	
C3	4·61	19·97	312	309	284	229	226
C4	5·05	21·54	321	303	292	229	226
C5	5·19	22·03	331	304	288	231	226
C6	7·20	28·59	381	303	292	231	220
C7	9·33	34·68	433	302	278		220
C8	9·76	35·83	450	303	279		
C9	11·04	39·05	489	455	303	274	
C10	11·86	41·03	523	466	302	289	
C11	12·87	43·26	543	473	303	281	
C12	14·27	46·21	564	482	304	272	
C13	15·44	48·52	575	486	305		
Purest possible NaSn, mean of two determinations			578	483			

TABLE II.

Alloys of Intermediate Composition.

No. of alloy.	Sodium. % by weight.	Sodium. Atomic %.	Arrests on cooling curve. Primary.	Arrests on cooling curve. Second.	Arrests on cooling curve. Third.
X1	27·22	65·88	466°	433°	
X2	25·46	63·81	449	435	
X3	25·75	64·15	438	432	
X4	23·96	61·93	443	441	
X5	23·33	61·10	448	441	
X6	23·18	60·90	450	430	335°
X7	22·75	60·31	457	425 †	336
X8	22·60	60·11	458	429	358
X9	21·62	58·73	473	435	356
X10	20·88	57·66	480		352
X11	19·98	56·31	— *	479 & 469	349
X12	19·53	55·61	529	479 & 471	348
X13	18·47	53·90	559	478	340
X14	17·60	52·43	574	481 & 483	355

* In this alloy the primary arrest was too slight to be located accurately.
† Marked supercooling and recalescence.

of the alloy, and to estimate the composition from the weights of sodium and tin used. When the sodium was cut under petroleum, quickly dried in filter paper, and at once corked up in the hard-glass tube, the sodium contents of the alloys determined by analysis were about 1% less than those calculated from the weighed quantities over the range 30—44% of sodium. In order to reduce the loss by oxidation, the apparatus shown in Fig. 1 was used: the sodium was placed in the upper tube which stands on top of the weighed hard-glass tube. The whole was filled with nitrogen, and then on heating it was possible, by gently tapping the tube, to filter the sodium into the lower tube, leaving the skin of oxide in the upper. In this way the sodium could be weighed without any oxidation, and since, for these sodium-rich alloys, larger quantities of sodium are used at lower temperatures, it is unlikely that the true composition of the alloy differed by more than a few tenths of a unit % from that calculated from the weighed amounts.

Results.

The experimental results can conveniently be divided into three sections. In order to save space the system of Heycock and Neville is adopted: an alloy described as, *e.g.*, "alloy 24·5" means one containing 24·5 *atoms* % of sodium. The results of the cooling-curve experiments are given in Tables I—III, and are plotted in Fig. 2; Fig. 3 shows the tin-rich end of the diagram on an enlarged scale.

FIG. 3.

The Equilibrium Diagram of the System Sodium–Tin: Tin-rich Alloys.

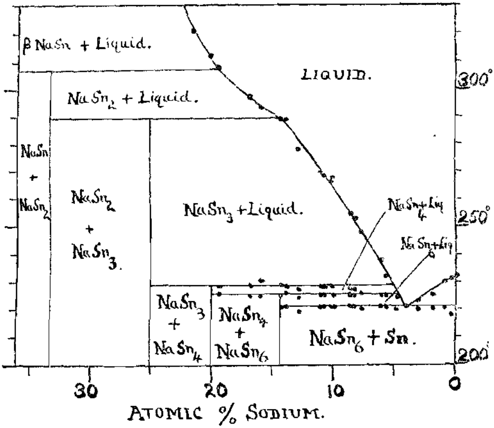


TABLE III.

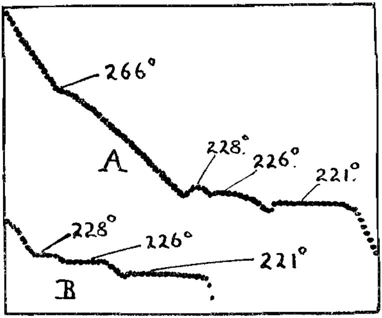
Sodium-rich Alloys.

No. of alloy.	Sodium. % by weight.	Sodium. Atomic %.	Arrests on cooling curve. Primary.	Arrests on cooling curve. Second.	Arrests on cooling curve. Third.
Z1	100	100	97°		
Z2	90·03	97·90	290	97°	
Z3	79·36	95·20	333	96	
Z4	63·69	90·06	367	97	
Z5	52·39	85·04	391	97	
Z6	48·69	83·05	398	97	
Z7	45·59	81·12	406	96	
Z8					
Purest possible Na_4Sn.	Mean of two determinations.	80·0	407–408		
Y1	40·86	78·10	419	407	370°
Y2	39·14	76·85	430	406	368
Y3	36·55	74·84	449	408	364
Y4	33·49	72·21	469	404	377
Y5	31·27	70·13	476	403	
Y6	28·64	67·43	478		
Y7	[illegible]				
Purest possible Na_2Sn		66·67	478		

I. *Tin-rich Alloys.*

When sodium is added to tin, the liquidus falls to a eutectic point at 220—221°, the eutectic composition being 4 atoms % of sodium (Mathewson gives 220° for this arrest). From this point the liquidus rises steeply with various breaks (see later) to a well-defined maximum at 50 atoms % corresponding to NaSn. According to Mathewson this compound is in equilibrium with liquid from its melting point down to 305°, at which temperature the compound $NaSn_2$ is formed by a peritectic reaction between NaSn and liquid. The compound

FIG. 4.



Examples of cooling curves for tin-rich alloys. Curve A shows that for loy 10·19. This is typical of unstirred alloys at normal rates of cooling, owing the supercooling of the 228° arrest and also of the eutectic at 221°. ırve B shows the lower part of the cooling curve of an alloy of almost the ıme composition, the curve being taken at a slower rate of cooling, and with gorous stirring of the alloy. In this case the supercooling of the 228° arrest prevented, and that of the eutectic is greatly reduced. In both curves the ·esence of two arrests besides that of the eutectic is made clear.

aSn_2 was described as undergoing a " transformation " extending ver the range 220—225°, and its low-temperature polymorphic ırm was regarded as forming one of the constituents of the 220° ıtectic, the other constituent being pure tin.

The present author's cooling curves at once showed that this transformation " of Mathewson was in reality composed of two stinct arrests, one at 225—226°, and the other at 228—229°. t normal rates of cooling the 229° arrest usually showed under-ıoling followed by recalescence, but even so the double nature of ıe arrest was apparent, whilst by using very slow cooling with

vigorous vibration of the tube containing the alloy, the two arrests could be obtained quite distinct, and with no appreciable under-cooling. Examples of these curves are shown in Fig. 4.

From 228°, the liquidus rises steeply to 289°, where a break occurs. In agreement with this, it was found that the cooling curves showed an arrest at this temperature in addition to their primary arrests. This arrest, which escaped Mathewson's notice, was always slight, and was apt to be masked by the much more pronounced arrest at 307°. The arrest found by Mathewson at 305° was confirmed, and, as will be shown later, his interpretation of it as due to the formation of the compound $NaSn_2$ is correct. The true temperature of this arrest, as given by very slow rates of cooling or by vigorously stirred alloys at normal rates of cooling, was 307°, but at normal rate of cooling the arrest is apt to show under-cooling, and may occu at any temperature between 300° and 307°.

None of the arrests at 307°, 289°, 229°, or 226° corresponded t an alloy freezing at constant temperature, but all were due to peri tectic reactions, and these never reached true equilibrium in th cooling-curve experiments owing to a sheath of the secondary soli being formed round the primary solid and so preventing the latte from further action with the liquid. Consequently, alloys whic began to freeze above 307° showed the whole series of these arrest in the cooling curves, and only became completely solid below th eutectic temperature at 220°. This was confirmed by the micr scopic examination of the cooling-curve ingots, which showed t solid adjoining the eutectic to consist of a whole series of laye which became more and more reactive as the centre was approache indicating a series of compounds in which the sodium conte increased towards the interior.

As these transformations never attained true equilibrium, t only chance of finding the compositions of the various phases w to prepare and anneal chill castings. Two series of experimer were carried out in which the alloys were annealed for 17 days 200°, and for 4 weeks at 210°, respectively. The results are sho in Table IV and may be summarised as follows. No solid soluti in tin could be detected. Even the alloy 0·52 showed two c stituents quite clearly after annealing. With increasing sodi content the tin was gradually replaced by a constituent which denoted by α. This was only slowly oxidised in air, and tarnis to a characteristic brownish colour with a curious shining appe ance. Alloy 14·05 consisted almost entirely of this constitu with traces of free tin, showing that the phase must contain sligh more sodium than 14·05 atoms %. Alloys 14·21 and 14·41 sho almost entirely α, with traces of a more reactive constituent in s

TABLE IV.

Details of annealing experiments.

Temp. of annealing.	Time of annealing.	Compositions of alloys annealed. (Na, atoms %).	Notes.
200°	17 days	0·52, 1·23, 3·02, 10·23, 11·13, 12·99	Free tin with increasing amounts of $NaSn_6$. All chill cast.
210	28 ,,	12·99, 13·81, 14·05, 14·21, 14·41, 15·26	See pp. 954 and 957. All chill cast.
200	17 ,,	16·70, 18·61	$NaSn_6$ and "spotted tarnish" constituent.
210	28 ,,	16·70, 18·61	$NaSn_6$ and "spotted tarnish" constituent. All chill cast.
210	28 ,,	19·97, 20·47, 21·03	See pp. 956 and 957. All chill cast.
210	28 ,,	21·03	$NaSn_4$ ("spotted tarnish" constituent) and $NaSn_3$. Chill cast.
200	17 ,,	22·03	
200	17 ,,	24·97	
210	28 ,,	24·97, 25·34, 25·37, 25·89	See p. 957. Chill cast.
210	28 ,,	26·28, 30·74, 31·38	$NaSn_3$ with increasing amounts of $NaSn_2$. Chill cast.
210	28 ,,	33·77, 33·96, 37·49, 38·67	$NaSn_2$ with increasing amounts of NaSn. Chill cast.
210	14 ,,	48·52	These experiments were made to see if there were any signs of solid solutions in the compounds of intermediate composition, and to see the effect of annealing Na_4Sn_3 below the transformation temperature. As no indication of solid solubility was obtained, chill castings were not prepared on account of the dangerous manipulation.
330	14 ,,	52·43, 56·31, 57·66, 65·88, 67·43, 78·10	
330	14 ,,	74·42, 76·26, 77·90	See p. 961.

parts, and a very little free tin in some areas, whilst alloy 15·26 showed α and a more reactive constituent, with a few areas in which traces of free tin could be seen. From this it is concluded that the constituent α is the compound $NaSn_6$ (14·3 atoms % of sodium), and that no appreciable solid solution exists, since no range of homogeneous alloys was observed. This last conclusion is supported by the fact that, even after 4 weeks' annealing, the alloys of composition very near $NaSn_6$ showed traces of both more and less reactive constituents, indicating that equilibrium had not

been completely reached, such slowness of reaction being characteristic of cases where no solid solution exists. Since the alloys annealed for 2 and for 4 weeks showed no differences, the annealings were stopped, as the work shows conclusively that the variation (if any) must be considerably less than 1 atom %. Fig. 5 shows alloy 14·4 after 4 weeks at 210°, consisting almost entirely of α with traces of a darker constituent.

To confirm this conclusion some of these annealed alloys were quenched from temperatures between 220° and 230°; the results are shown in Table V. In all these cases the inevitable handling of the alloy caused a thin surface film to oxidise and melt above 220°, but this was ignored. These experiments showed that from 220° to 224° the phase in equilibrium with the liquid was the constituent α, but that at 227° a new darker-etching phase was in equilibrium with the liquid. This is well shown in Fig. 6, which represents alloy 13·81 quenched from 227°: dark compact crystals of the new constituent, which we may call β, are surrounded by a thin film of light-etching α formed during the quenching, these being embedded in eutectic, the structure of which is not resolved at this magnification. From the quenching experiments we may therefore conclude that the α, or $NaSn_6$, is formed by a peritectic reaction between 224° and 227°, and this clearly corresponds to the 226° arrest found on the cooling curves.

From alloy 14·41, with increasing quantities of sodium the alloys consisted of $NaSn_6$ with increasing amounts of the darker-etching constituent β, which etched in air or under oil with a curious "spotted tarnish" effect. Alloy 19·97 consisted almost entirely of this constituent, whilst alloy 20·47 showed chiefly this constituent with some of a more reactive phase, which we may call γ, in the grain boundaries. It was difficult to decide whether this "spotted tarnish" constituent (see Fig. 7) was really composed of one phase or two, but it is considered to be a single phase on the following grounds: (1) The fineness of the tarnish pattern appeared to vary with the conditions of formation (*e.g.*, tarnishing under oil or in air). (2) In alloy 21·03 a more reactive phase was undoubtedly present in the grain boundaries; if the "spotted tarnish" constituent were in reality due to two phases, this would indicate that the alloy had three phases, and had not yet reached equilibrium, and if this were so, we should not expect to find the most reactive constituent in the grain boundaries, but rather as unchanged cores in the middle of the grains. (3) The dark-etching crystals shown in Fig. 6 were themselves etched with a distinctly spotted appearance, although here there can be no doubt that they represent the phase in equilibrium with the liquid. (4) Finally, if the effect indicated two phases, it

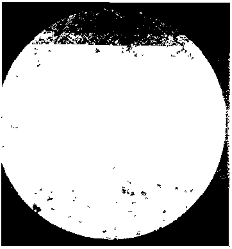


FIG. 5.—Alloy 14·4 annealed for 4 weeks at 210°.
Magnification, 300.

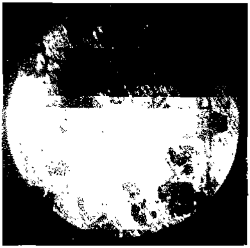


FIG. 6.—Alloy 13·81, annealed for 4 weeks at 210°, then heated to 227°, and quenched in oil.
Magnification, 150.

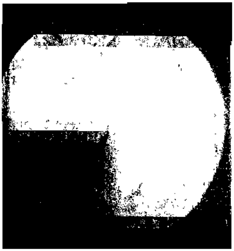


FIG. 7.—Alloy 20·47 after annealing for eeks at 210°, showing the "spotted tarnish" stituent with small amounts of a more ctive phase.
Magnification, 150.

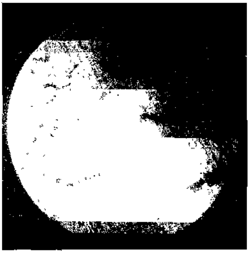


FIG. 8.—Alloy 25·34 after annealing for 4 weeks at 210°, showing chiefly γ ($NaSn_2$) with traces of a more reactive constituent.
Magnification, 150.

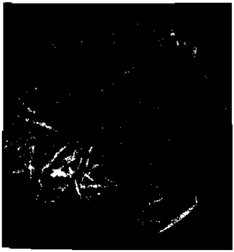


FIG. 9.—Alloy 76·26, chill cast, showing Na_3Sn (white) and Na_4Sn (black).
Magnification, 150.

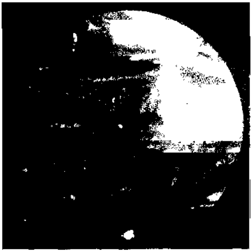


FIG. 10.—Alloy 76·26 after annealing for 2 weeks at 330°, showing chiefly Na_3Sn, with holes, and fine dark lines which are probably Na_4Sn.

would be a remarkable coincidence that it should reach a maximum at exactly 20 atoms % of sodium.

TABLE V.

Results of quenching experiments on tin-rich alloys.

(All these experiments refer to chill-cast alloys which had received a preliminary annealing of either 17 days at 200° or 28 days at 210°.)

Comp. of of alloy (atomic % *Na*).	Quenching *temp.*	Whether melted *or not.*	*Notes.*
12·99	222°	Very slightly melted.	$NaSn_6$ in equilibrium with *liquid.*
14·41	222	Solid.	
14·41	*226*	,,	
13·81	224	Very slightly melted.	$NaSn_6$ in equilibrium with *liquid.*
13·81	227	Melted.	Dark crystals in equilibrium with liquid.
14·41	230	,,	,, ,,
19·97	230	,,	,, ,,
21·03	230	Slightly melted.	,, ,,
19·97	227	Solid.	
16·70	227	Melted.	,, ,,
24·97	230	Solid.	
25·89	230	,,	

NOTE.—*In the above experiments a thin surface layer of the alloy always* melted above 220° owing to the inevitable slight oxidation during handling. This has been ignored. There was some slight evidence that the dark crystals in equilibrium with the liquid at 230° were different in shape from those in equilibrium at 227°, but this could not be considered conclusive, although it is *in agreement with the author's diagram.*

On these grounds the phase β was considered to be $NaSn_4$, and this was confirmed by the quenching experiments (Table V), which showed alloy 19·97 to be solid at 227°, but to have melted at 230°. *The compound* $NaSn_4$ *thus corresponds to a peritectic reaction between these two temperatures, agreeing with the 229° arrest on* the cooling curves.

With increasing sodium content, the alloys consisted of $NaSn_4$ together with the more reactive phase γ. After 4 weeks at 210°, alloy 24·97 consisted almost entirely of γ, with occasional traces of both more and less reactive phases in some areas, but with large patches entirely homogeneous. Alloy 25·34 consisted chiefly of the new phase γ with a little of a still more reactive phase in the grain boundaries, as shown in Fig. 8. On these grounds the constituent γ is considered to be the compound $NaSn_3$, and in agreement with this the quenching experiments showed alloys 24·97 and 25·89 to be solid at 230°. No evidence could be found for the existence of any solid solution. As shown in Fig. 8, $NaSn_3$ etches in air or under oil with a very much more finely divided tarnish pattern than $NaSn_4$.

On further raising the sodium content, the annealed alloys consisted of $NaSn_3$ with increasing amounts of a more reactive constituent which was readily identified as $NaSn_2$, reported by Mathewson. This compound takes a very high polish if kept out of contact with air. There again appears to be no appreciable region of solid solubility.

There is thus one phase corresponding to each arrest on the cooling curves, and this fact gives considerable support to the results obtained in this part of the diagram, which is much more complex than previously supposed. Mathewson only examined nine alloys between 0 and 33·3 atoms % of sodium, and as he did not prepare chill castings for annealing purposes, his work could not have led to the identification of the numerous phases concerned. The present work also explains why the composition–potential curves of Kremann and Gmachl-Pammer did not fit in with the theoretical requirements of the old diagram in this region, for their alloys too were not annealed.

II. *Alloys of Intermediate Composition.*

The compound NaSn corresponds to a well-defined maximum on the liquidus, the freezing point being determined as 578° from two closely-agreeing measurements; the value found by Mathewson was 575°. This compound, as stated by Mathewson, undergoes a transformation, the true temperature of which was determined as 483°, whereas he gave 480—483°. This transformation usually shows marked undercooling, and the true temperature can only be determined by reducing the rate of cooling to about 1° per minute. Mathewson's identification of this change as a polymorphic transformation of the compound NaSn appears to be correct for the following reasons. (1) The change is shown by alloys on both sides of the maximum on the freezing-point curve, and hence it is very improbable that it is due to a reaction between NaSn and liquid to form a new phase, since there would have to be two such phases, one containing more and one less sodium than the compound NaSn, and it would be a very remarkable coincidence if both these reactions occurred at the same temperature. (2) The fact that Kremann and Gmachl-Pammer (*loc. cit.*), with slowly cooled specimens, found a break at 50 atoms % in the potential–composition curves, indicates that one form of this compound exists at low temperatures. On these grounds, the line *AB* is drawn in *Fig. 2* as showing the transformation from the high-temperature (α-) form of NaSn to the low-temperature (β-) form.

With higher sodium content, the liquidus falls steeply until there is a distinct break at 479—480°, at which the compound Na_4Sn_3

freezes at constant temperature (Mathewson gave 478°). The cooling curves in this region are apt to be very complex on account of the supercooling shown by the change α-NaSn ⇌ β-NaSn, since if this cools below 479°, the compound Na_4Sn_3 may begin to freeze, and then the NaSn transformation takes place with a rise in temperature. The present work, however, completely confirmed Mathewson's conclusion that the 483° and 479° transformations were distinct, although Kremann and Gmachl-Pammer had doubted this.

From here, the liquidus falls to a eutectic point at 62 atoms % of sodium, and 441° (Mathewson gave 61·7% and 440°). This arrest is prone to show under-cooling, and, with normal rates of cooling, may occur at any temperature between 430° and 440°. From the eutectic the liquidus rises steeply to a maximum at 478°, at which the compound Na_2Sn freezes at constant temperature; the value found by Mathewson was 475°.

According to Mathewson the compound Na_4Sn_3 underwent a polymorphic change in the range 320—350°, and, in agreement with this, the author's cooling curves showed arrests in this region. These transformations exhibited marked hysteresis on both heating and cooling curves, and even when the rate of change of temperature was reduced to 1° per minute, there was still a difference of 10° between the values given on heating and cooling curves; the mean values from curves of this nature with two different alloys were 358° and 357°. In order to determine the nature of this change, alloys were annealed for 2 weeks at 330°, *i.e.*, just below the transformation temperature. If Mathewson's interpretation of the transformation as a polymorphic change of Na_4Sn_3 be correct, the alloy 57·66, on annealing at 330°, should show almost all one constituent (the supposed low-temperature form of Na_4Sn_3) with a slight excess of Na_2Sn. Actually, however, it showed a finely divided two-constituent structure characteristic of the changes in which one phase on cooling splits into two phases. This was confirmed by the microstructure of the other slowly-cooled ingots in this region, for in all these the phase which, according to Mathewson, should have been homogeneous Na_4Sn_3, possessed this finely-divided eutectoid-like structure. On these grounds, therefore, the transformation at 357° is regarded, not as a polymorphic change of Na_4Sn_3, but as the decomposition of this compound on cooling into two other phases; and since, on annealing at 330°, all the alloys between NaSn and Na_2Sn showed two constituents, it is concluded that the Na_4Sn_3 splits up into NaSn and Na_2Sn, the transformation at 357° corresponding to the change

$$Na_4Sn_3 \underset{}{\overset{\text{(cooling)}}{\rightleftharpoons}} 2NaSn + Na_2Sn.$$

This also explains why Kremann and Gmachl-Pammer (*loc. cit.*) using slowly cooled alloys, found no evidence for the existence of the compound Na_4Sn_3 at the ordinary temperatures at which their measurements were made.

Apart from this one point, the present results are in good agreement with those of Mathewson, for alloys within this range.

III. *Sodium-rich Alloys.*

Over the range 66·6—100 atoms % of sodium, the author's determination of the liquidus agrees remarkably well with that of Mathewson, the curve falling from the freezing point of Na_2Sn to 408° (Mathewson 405°) at which the compound Na_4Sn freezes at constant temperature; from here the liquidus falls steeply to the melting point of pure sodium. Mathewson, however, concluded that the liquidus and solidus did not exactly coincide at his 405° transformation line, but that the composition of the liquid was here 80·8 atoms % of sodium, the compound thus melting over a slight range of temperature. The present work does not confirm this. The smooth curves through the three points on either side of the compound meet almost exactly at the 80% line. That the solidus and liquidus meet at this point is further shown by the fact that the 97° arrest, at the melting point of sodium, was shown by alloys 83·05 and 81·12, but not by alloy 80·0 or 78·10. If the compound Na_4Sn did not melt at constant temperature, but corresponded to a peritectic reaction at 408°, we should not expect this to proceed to complete equilibrium in the cooling-curve experiments (owing to the effect of the film of solid first formed round the primary crystals) and we should expect to find traces of the 97° arrest continuing in the last two alloys in the same way that the low-temperature arrests persisted in the tin-rich alloys. The evidence is therefore that the compound Na_4Sn melts at constant temperature.

On the other hand, the author's cooling curves showed a brief arrest in the region 360—380° for alloys between 66·6 and 80 atoms % of sodium, and from slow heating and cooling curves the true temperature of this was found to be 377° (heating, 380°; cooling 374°). This was not given by either pure Na_4Sn or pure Na_2Sn and the only reasonable explanation seems to be that at this temperature these two compounds react to form another phase of intermediate composition. The arrest was a maximum between 75 and 80 atoms % of sodium, indicating that the new phase might be Na_3Sn, and with very great difficulty chill castings were prepared in this range of composition, and were annealed for 2 weeks at 330°. Fig. 9 shows the casting of alloy 76·26. Here will be seen light needles (indicating plate-like crystals) of Na_2Sn in a ground mass of

Na_4Sn. In spite of the great reactivity of its constituents, this alloy could be photographed under an oil film at any time up to 50 seconds after polishing, although the structure of the Na_4Sn could never be seen. After annealing, the whole structure had changed, no Na_2Sn could be seen, and the alloy was so very much more reactive that, even under oil, it was almost impossible to photograph it before the whole surface appeared black. After many failures, however, Fig. 10 was obtained; the structure here shows numerous holes (indicating a volume change), and chiefly one constituent appearing dark grey in the photograph, and small dark lines which are either a second more reactive constituent or else fine cracks. The white spots are bubbles of hydrogen. On the other hand, alloy 74·42 showed some of the light Na_2Sn left over after annealing, whilst alloy 77·9 looked very much like Fig. 10 with more of the fine dark lines. On these grounds, therefore, it is considered that the transformation at 377° corresponds to the combination of Na_4Sn and Na_2Sn to form Na_3Sn, which decomposes to its constituent compounds on heating through the transformation temperature. That Na_3Sn forms little or no solid solution is shown by the fact that the annealed alloy 74·42 showed some Na_2Sn to be present, whilst if the fine dark lines in alloys 76·26 and 77·90 indicate Na_4Sn, it is clear that there is little solid solubility on the sodium side. It must be admitted that this evidence is not entirely conclusive, but it is not unsatisfactory in view of the intense reactivity of these alloys, for they explode when dropped into water, and even under oil become black within 30 seconds.

The annealing experiments failed to show any solid solutions in the compound Na_2Sn, or on the tin side of Na_4Sn. Alloy 81·12 showed a clear arrest at 96° on the cooling curve, indicating that little or no solid solubility exists on the sodium side of Na_4Sn, but as this alloy is partially liquid above 97° annealing experiments were not carried out.

Discussion.

The system sodium–tin contains the compounds Na_4Sn, Na_3Sn, Na_2Sn, Na_4Sn_3, NaSn, $NaSn_2$, $NaSn_3$, $NaSn_4$, and $NaSn_6$. All these are definitely metallic, and conduct electricity, the least metallic-looking being Na_2Sn, which is bluish-black and closely resembles the bluish-black Mg_2Sn (probably Mg_4Sn_2), as has been previously pointed out by the author. The density of Na_2Sn was determined as 2·94 by using xylene as the immersion fluid, and a stoppered pyknometer.

As the author has previously suggested, the metallic properties of compounds of this nature indicate that some of the valency electrons are not bound into stable octets, or other groupings,

but remain more loosely held. Of the compounds discovered, $NaSn_6$ and $NaSn_4$ readily suggest themselves as co-ordination compounds of the sodium *ion*, with 6 and 4 atoms, respectively, surrounding the positively charged ion, and thus leaving the one free valency electron over to give the substance its metallic properties. For the other compounds, electronic structures must remain speculative until methods have been devised for determining the true molecular weights and the number of " free " electrons present, or alternatively, until the crystal structure has been investigated.

Summary.

The equilibrium diagram of the system sodium–tin has been investigated by thermal and microscopic methods. More than 60 alloys have been annealed or quenched under different conditions, and 63 independent cooling-curve experiments have been carried out.

The system has been shown to be very complex, and to contain the nine compounds Na_4Sn, Na_3Sn, Na_2Sn, Na_4Sn_3, NaSn, $NaSn_2$, $NaSn_3$, $NaSn_4$, and $NaSn_6$.

Of these, the compounds Na_2Sn (m. p. 478°) and NaSn (m. p. 578°) correspond to maxima on the liquidus, and melt at constant temperatures. The compound NaSn undergoes a polymorphic transformation at 483°.

The compounds Na_4Sn (m. p. 408°) and Na_4Sn_3 (m. p. 479°) also melt at constant temperatures, but correspond to breaks in the liquidus and not to maxima. The compound Na_4Sn_3 is only stable above 357°, and on cooling below this temperature it splits up into the compounds Na_2Sn and NaSn, the reverse change taking place on heating above 357°.

The compound Na_3Sn exists only in the solid state, and on heating above 377° it decomposes into a mixture of the compounds Na_4Sn and Na_2Sn.

The compound $NaSn_2$ is formed at 307° by a reaction between the compound NaSn and liquid; the compound $NaSn_3$ is formed at 289° from $NaSn_2$ and liquid; the compound $NaSn_4$ is formed at 229° from $NaSn_3$ and liquid; and the compound $NaSn_6$ is formed at 226° from $NaSn_4$ and liquid. None of these compounds melts at a constant temperature, but all correspond to peritectic reactions indicating extensive decomposition on melting.

No evidence has been found for the existence of any solid solutions. The results are discussed in the light of previous work.

The author expresses his gratitude to Professor W. H. Perkin, F.R.S., for having given facilities for metallurgical work to be

carried out in his laboratory, and to Mr. J. J. Manley for the loan of a vacuum pump. He also acknowledges his indebtedness to the Government Grant Committee of the Royal Society and to Messrs. Brunner Mond and Co. for grants towards the cost of this and other research work.

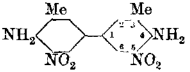
MAGDALEN COLLEGE, OXFORD. [*Received, February 16th*, 1928.]

CXXVI.—*Orientation Effects in the Diphenyl Series. Part VI. The Supposed Isomerism of the Dinitrotolidines.*

By RAYMOND JAMES WOOD LE FÈVRE and EUSTACE EBENEZER TURNER.

IN 1914, Cain and Micklethwait (J., **105**, 1442) described the discovery of isomeric dinitrotolidines corresponding to the 3 : 3′- and 3 : 5′-dinitrobenzidines they had previously isolated. They also described four isomeric dinitrotolidines in which the nitro-groups occupied in each case two of the four positions 2, 2′, 6, and 6′.

Gerber (*Ber.*, 1888, **21**, 746) had already shown that when diacetyl-*o*-tolidine was nitrated, the main product after hydrolysis had m. p. 266—267° and was the dinitro-compound (I), its constitution being based upon its convertibility into a quinoxaline.

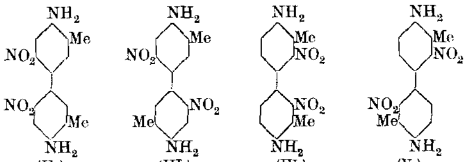


(I.)

Cain and Micklethwait stated that they set out in the hope of isolating a second dinitro-compound, corresponding to Bandrowski's base, regarded by Cain as 3 : 3′-dinitrobenzidine. In attempting to repeat Gerber's work, they apparently were successful, and described the isolation of what they called *o*-dinitrotolidine II in addition to Gerber's compound, which they designated *o*-dinitrotolidine I. Cain and Micklethwait also nitrated diphthalyl-*o*-tolidine, evidently hoping to obtain *o*-dinitrotolidine II in better yield. Instead, they described the isolation of four isomeric *m*-dinitrotolidines, to which they gave formulæ (II) to (V).

One of these compounds had previously been obtained by Gerber (Diss., Basel, 1889) by nitrating *o*-tolidine sulphate. . Gerber regarded his substance as II, and was correct in so doing, for later Täuber and Löwenherz (*Ber.*, 1891, **24**, 1033) succeeded in converting it

into a diaminodimethylcarbazole, a conversion incidentally repeated and confirmed by Cain and Micklethwait.


(II.) (III.) (IV.) (V.)

Cain and Micklethwait also described the conversion of *o*-dinitrotolidine II into *o*-dinitrotolidine I, and thus added very considerably to their evidence for 3 : 3′–3 : 5′ isomerism.

As a result of our previous discovery (J., 1926, 1759) that Cain's space isomerides were actually position isomerides, we re-investigated the dinitrotolidine question. We find that when diacetyl-*o*-tolidine is nitrated, etc., two products can indeed be isolated, but that one is formed only in small quantity, and although it melts, as Cain and Micklethwait stated, at about 202—203°, it is in reality an impure specimen of 6 : 6′-dinitro-*o*-tolidine, since it may be converted into 4 : 4′-*dibromo*-6 : 6′-*dinitro*-3 : 3′-*dimethyldiphenyl*, a substance which does not react with boiling piperidine.

When investigating Bandrowski's dinitrobenzidine, we showed that this compound was formed almost quantitatively by the nitration of 2-nitrodiacetylbenzidine. The nitration of the corresponding tolidine derivative, *viz.*, 6-nitrodiacetyl-o-tolidine, however, under similar conditions gives the 6 : 6′-dinitro-compound.

We have confirmed the structure of Gerber's dinitro-*o*-tolidine (obtained by nitration of diacetyltolidine) by converting it into 4 : 4′-*dibromo*-5 : 5′-*dinitro*-3 : 3′-*dimethyldiphenyl*, which readily reacts with boiling piperidine to give 5 : 5′-*dinitro*-4 : 4′-*dipiperidino*-3 : 3′-*dimethyldiphenyl*.

There are three other observations made by Cain and Micklethwait which also require explanation. First, they isolated from the product of hydrolysis of dinitrodiacetyltolidine " a yellowish-brown residue." They said further : " It was found, however, that if this material was crystallised from amyl alcohol further amounts of the isomeric bases could be obtained. The existence of this yellowish-brown substance and its general behaviour indicate possibly that we are here dealing with bases and their internal salts." There is little doubt that the yellowish-brown product was a mixture of dinitrotolidine with dinitrodiacetyltolidine which had escaped hydrolysis

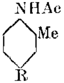
(compare the hydrolysis of nitrophthalylbenzidine, Le Fèvre and Turner, this vol., p. 245). Secondly, Cain and Micklethwait heated their *o*-dinitrotolidine II with acetic acid and acetic anhydride, and eventually isolated a little diacetyl-*o*-dinitrotolidine I. This is now explained, since " base II " was a mixture containing a considerable quantity of base I. Thirdly, these authors reduced both *o*-dinitrotolidine I and II and condensed the resulting tetra-amines with benzil. In both cases one and the same quinoxaline was obtained, and although this to Cain and Micklethwait implied constitutional as distinct from configurational identity, their result is now an experimental necessity, since *o*-dinitrotolidine I is present in the supposed isomeride.

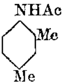
The nitration of diacetyl-*o*-tolidine (VI) may be compared with that of aceto-1 : 3 : 4-xylidide (VII). The latter compound is converted by nitric acid into the 5-nitro-derivative, and by nitric and sulphuric acids mainly into the 6-isomeride (Hofmann, *Ber.*, 1876, 9, 1295; Noelting and Collin, *Ber.*, 1884, **17**, 265).

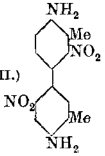
We have not investigated Cain and Micklethwait's four " isomerides " of the meta-series, but a sufficient explanation of these authors' results is that the four compounds are not (II—V), but are (II), (IV), (VIII) and (IX). Cain and Micklethwait appear to have overlooked the possibility of (VIII) being formed, although it is more to be expected than (IV). Their *m*-dinitrotolidine I certainly has formula (II), for the reasons stated above. Their *m*-dinitrotolidines II and IV were converted into compounds which gave correct analyses for carbazoles, agreeing with the present formulæ (IV) and (VIII). Cain and Micklethwait had insufficient of the fourth isomeride (*m*-dinitrotolidine III) for an attempt to convert it into a carbazole, but in view of the very small amount of it obtained it is reasonable to regard it as (IX). Moreover, Cain and Micklethwait's paper contains very little real evidence upon which constitutions of their *m*-dinitrotolidines II, III and IV could soundly be based. No yields are quoted in the paper, and the amount of material available for analysis appears to have been very small.

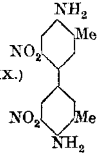
The 4 : 4′-dibromo-6 : 6′-dinitro-3 : 3′-dimethyldiphenyl referred to above is also obtained by nitrating 4 : 4′-dibromo-3 : 3′-dimethyldiphenyl; similarly, 4 : 4′-dichloro-3 : 3′-dimethyldiphenyl nitrates to give *4 : 4′-dichloro-6 : 6′-dinitro-3 : 3′-dimethyldiphenyl*. 4 : 4′-Dihalogenodiphenyls nitrate unsymmetrically (Dennett and Turner, J., 1926, 476), and it is interesting to compare the nitration of the dihalogenoditolyls now described with such nitrations as those of 1 : 2 : 4-trichlorobenzene, 3 : 4-dichloroacetophenone, and 3 : 4-dichloronitrobenzene (all nitrating in position 5). All these cases are illustrations of the apparently general tendency for the formation

of 1 : 2 : 4 : 5-compounds rather than the 1 : 2 : 3 : 4- or 1 : 2 : 3 : 6-isomerides.

(VI.) 

(VII.) 

(VIII.) 

(IX.) 

EXPERIMENTAL.

Diacetyl-o-*tolidine*.—Acetic anhydride (60 c.c.) was added slowly to a gently boiling solution of *o*-tolidine (106 g.) in acetic acid (300 c.c.). The product was crystallised from phenol–alcohol.

Nitration of Diacetyl-o-*tolidine*.—Diacetyltolidine (35 g.) was slowly added to nitric acid (*d* 1·5), the temperature being kept below 0°. The yellow paste obtained by pouring the mixture on crushed ice was treated with steam to remove nitric acid, well washed with boiling water, and dried at 100°. Hydrolysis was effected with concentrated sulphuric acid, the procedure usual in this series being followed.

The diluted acid solution was filtered after 12 hours, and the sulphate obtained was ground under aqueous ammonia. After washing and drying, 16 g. of a red powder were obtained, m. p. below 210°. The m. p. was raised to 261° by the first crystallisation from phenol–alcohol, and after two further crystallisations 7 g. of pure 5 : 5′-dinitro-*o*-tolidine, m. p. 268—269°, were obtained.

o-*Dinitrotolidine II*.—The mother-liquors from all the above crystallisations were mixed with an excess of sodium hydroxide solution, the more soluble sulphates being obtained as bases, and the excess of phenol was removed. The reddish-brown product was washed with hot water, dried at 100°, and extracted with 150 c.c. of benzene in a Soxhlet apparatus. After cooling and filtering, the clear benzene solution was evaporated to dryness. A bright red, brittle glass was obtained, which appeared to crystallise on being stirred with alcohol. This product (about 1·5 g.) had a m. p. of 200—205° and a definitely crystalline appearance and did not undergo any change of m. p. when twice recrystallised from benzene. It (0·8 g.) was bisdiazotised, and the diazoperbromide prepared in the usual way. Decomposition with boiling glacial acetic acid gave a cream-coloured product ; this, after three crystallisations from glacial

acetic acid, formed long, thin needles (m. p. 270°) which slowly reacted with boiling piperidine. The identity of the dibromodinitroditolyl was proved by a mixed m. p. determination with authentic 4 : 4′-dibromo-5 : 5′-dinitro-3 : 3′-dimethyldiphenyl (see later).

The residues from the above benzene extraction changed from red to orange-yellow on drying—indicating the presence of a considerable quantity of 6 : 6′-dinitrotolidine. They were treated as above for *o*-dinitrotolidine II, but a pure product was not obtained. After several crystallisations from much glacial acetic acid, the dibromo-compound had m. p. about 230°. This, and the fact that boiling piperidine caused no change in the m. p. even after 1 hour, show it to be 4 : 4′-dibromo-6 : 6′-dinitro-3 : 3′-dimethyldiphenyl.

Nitration of 6-Nitrodiacetyltolidine.—The acetyl derivative was prepared by the method of Löwenherz (*Ber.*, 1892, **25**, 1032). 10 G. were slowly added to 100 c.c. of nitric acid (*d* 1·5) at 0° to –5°. After 1 minute, ice was added, and the white suspension was filtered off, washed, and hydrolysed with sulphuric acid. The reddish-brown product could not be crystallised from the ordinary solvents and therefore was extracted with benzene as described above. From the benzene extract no chemical individual could be isolated, but from the reddish-yellow (less soluble in benzene) residue, about 2·5 g. of 4 : 4′-dibromo-6 : 6′-dinitro-3 : 3′-dimethyldiphenyl were obtained by the perbromide method. The yield of the latter compound indicates that 6 : 6′-dinitrodiacetyltolidine is formed to a considerable extent in the nitration of 6-nitrodiacetyltolidine.

4 : 4′-*Dibromo-5 : 5′-dinitro-3 : 3′-dimethyldiphenyl.*—A solution of pure 5 : 5′-dinitrotolidine (7 g.) in 20 c.c. of concentrated sulphuric acid was bisdiazotised at –5° with 3·3 g. of sodium nitrite. After being poured on ice, diluted with water, and filtered, the mixture was treated with a solution of 5 c.c. of bromine in 15 c.c. of hydrobromic acid (*d* 1·49). Decomposition of the precipitated perbromide was effected in boiling glacial acetic acid, and the product, which was sparingly soluble in this solvent, had m. p. 269—271°. From much acetic acid, it crystallised in matted wads of pale yellow, hairy needles, m. p. 271—272° (Found : N, 6·9. $C_{14}H_{10}O_4N_2Br_2$ requires N, 6·5%).

4 : 4′-*Dipiperidino-5 : 5′-dinitro-3 : 3′-dimethyldiphenyl.*—The last-named compound, when gently refluxed for 1 hour with piperidine, dissolved, and the solution become filled with crystalline cakes of piperidine hydrobromide. Dilution with water gave a product which crystallised from acetic acid in bright yellow plates, m. p. 226—227° (Found : N, 13·0. $C_{24}H_{30}O_4N_4$ requires N, 12·8%).

4 : 4′-*Dibromo-6 : 6′-dinitro-3 : 3′-dimethyldiphenyl.*—A perbromide

displacement on 12 g. of 6 : 6′-dinitrotolidine gave 9 g. of a cream coloured substance, which crystallised from acetic acid in long needles, m. p. 230—233° (softening at 225°). Two further crystallisations did not raise the m. p. above 230—233° (Found : N, 6·7 Calc. : N, 6·5%).

4 : 4′-*Dichloro*-3 : 3′-*dimethyldiphenyl*.—*o*-Tolidine (90 g.) was bisdiazotised according to the directions of Schultz, Rhode, and Vicari (*Annalen*, 1907, **352**, 124) and the resulting solution was allowed to drop slowly into a vigorously stirred solution of cuprous chloride (from 240 g. of copper sulphate crystals) in 750 c.c. of concentrated hydrochloric acid, heated at 100°. Stirring was continued for ½ hour, and the reaction mixture allowed to cool overnight. The dark brown oil obtained was washed by decantation and extracted with benzene, the extract was washed repeatedly with sodium hydroxide solution and with water and dried over sodium sulphate, and the benzene was removed by distillation. The dichloroditolyl was collected at 310—320° (yield, 58 g.); after crystallisation from alcohol, it melted at 52—53° as stated by Schultz, Rhode, and Vicari.

4 : 4′-*Dibromo*-3 : 3′-*dimethyldiphenyl* was prepared by the usual method from 100 g. of *o*-tolidine, dissolved in 300 c.c. of concentrated hydrochloric acid diluted with 100 c.c. of water. The solution resulting after the addition of 70 g. of sodium nitrite (in 150 c.c. of water) was slowly added to a solution of cuprous bromide prepared with the aid of 90 g. of potassium bromide; the decomposition was vigorous. The reddish-brown oily product, after being washed in benzene solution with alkali, water, and dilute acid and dried over sodium sulphate, was distilled. The main fraction, b. p. 202—215°/20 mm., solidified on cooling, and after being crystallised from much alcohol, formed long, white needles, m. p. 63—64° (Stolle, *Ber.*, 1888, **21**, 1099, gives m. p. 58—59°).

Nitration of 4 : 4′-*Dichloro*-3 : 3′-*dimethyldiphenyl*.—Dichloroditolyl (6·2 g.) was slowly added to nitric acid (*d* 1·5; 100 c.c.), cooled in water. The mixture was heated at 100° for 10 minutes and poured into water. The cream-coloured, flocculent powder obtained gave yellow crystals, m. p. 165—170°, 201—202°, and 211—212°, respectively, after one, two, and three crystallisations from glacial acetic acid (Found : Cl, 20·4. $C_{14}H_{10}O_4N_2Cl_2$ requires Cl, 20·8%).

10 G. of 6 : 6′-dinitrotolidine were warmed with 50 c.c. of concentrated hydrochloric acid, and 50 c.c. of water were added when hydrochloride formation was complete. The whitish suspension was then bisdiazotised at 0°. The filtered solution was added to a suitable solution of cuprous chloride in hydrochloric acid. Normal procedure led to the isolation of a powder which, after three crystal-

lisations from glacial acetic acid, melted at 212° and was identical with the nitration product from the last experiment.

Nitration of 4 : 4′-Dibromo-3 : 3′-dimethyldiphenyl.—The dibromo-compound (5 g.) was slowly added to 35 c.c. of nitric acid (*d* 1·5), the temperature of which was kept below 20°. The addition of a little water then caused crystallisation to set in. The washed precipitate was extracted with hot glacial acetic acid (the extracts deposited crystalline material, m. p. 150—210°), and the almost insoluble residue was crystallised from a large bulk of glacial acetic acid. It was thus obtained as yellow needles, m. p. 228—230°, with slight previous softening. After three further crystallisations this m. p. was unchanged—it is difficult to account for an indefinite m. p. in the case of a compound of this type.

A mixed m. p. determination with the product obtained from a perbromide displacement on 6 : 6′-dinitrotolidine (above), however, showed that the two substances were identical.

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LONDON. [*Received, February 15th, 1928.*]

CXXVII.—*Observations on the Passivity of Metals.*

By ERNEST SYDNEY HEDGES.

THE question whether iron which has been dipped in concentrated nitric acid owes its chemical inertness to a protective film of oxide or to a change in the nature of the metal itself has long been a matter of controversy, but the isolation by Evans (J., 1927, 1020) of a film of ferric oxide on iron rendered passive by a variety of means leaves no doubt that in these cases the inertness is due to a protective film. Evans was unable, however, to isolate such a film on iron made passive by concentrated nitric acid, because of the spontaneous breakdown of the passivity after withdrawal of the metal from the nitric acid.

One of the objects of the present paper is to show, by the use of methods which do not involve the removal of the metal from the acid, that iron rendered passive by nitric acid also has a protective oxide film. If the passive metal is coated with an oxide film, it may be expected that this film will be washed or torn off when the metal is whirled rapidly in the liquid, so that the iron will become active and dissolve. On the other hand, according to the view advanced by Smits ("Theory of Allotropy," 1922, p. 345), the more rapid removal of ions from the metal by a high speed of rotation will produce a more violent disturbance of the inner equilibrium at the surface of the metal and the iron will tend to become more passive.

Further strong evidence for the existence of an oxide film on passive iron is afforded by the recent work of Freundlich, Patscheke, and Zocher (*Z. physikal. Chem.*, 1927, **128**, 321; *ibid.*, **130**, 289).

The Passivation of Iron by Nitric Acid.—The electrolytic iron used in these experiments was very kindly provided by Mr. U. R. Evans, and its manufacture and analysis have been described by him (*loc. cit.*). The surface of the metal had, however, become somewhat corroded by damp soda-lime, in which it had been packed: this was not a serious drawback for the present investigations. The material was cleaned in dilute sulphuric acid, and washed in water before use.

In order to conduct the "whirling" experiments under the most sensitive conditions, it was first necessary to determine the minimum concentration of nitric acid which would suffice to passivate the iron. At first, reproducible values were not obtained, but it was soon found that the iron should not be used too soon after being taken out of the sulphuric acid. In order to obtain reproducible values, the sheet of iron was dried, cut up into pieces 1 cm. × 1 cm., and kept for 24 hours before use. No doubt, the slight "air-passivity" soon reaches a constant value.

Another source of error was found to be that in solutions of nitric acid containing 7—14% of water (by vol.), the production of passivity depends on the rate at which the iron passes through the surface of the liquid: metal which was active as it passed through the surface became passive before it reached the bottom of the vessel. Reproducible results could be obtained only by throwing the metal forcibly through the liquid surface; in fact, if one piece of iron foil is gently dropped with its flat side to the liquid surface, and another piece is thrown edge-ways through the surface, the first piece dissolves with great vigour, whereas the second piece is unattacked. This phenomenon has its counterpart in the liquid-line corrosion observed when a metal is half-immersed in a corroding medium. This can be observed both in the present experiments and in anodic passivation. According to Evans (*loc. cit.*, p. 1036), this is to be explained by the protective film tending to leave the metal–liquid interface and collect at the liquid–air interface. Such an explanation seems to account for the present case, but it is doubtful whether it is generally applicable: in some cases it seems necessary to postulate an enhanced reactivity at a liquid surface (compare Hedges, J., 1926, 831). (As a further example of the modifying influence of a liquid surface, the author has recently observed that in crystallising mercuric iodide by cooling a hot saturated solution in potassium iodide, red crystals form on the bottom and sides of the beaker, but the crystals forming at the liquid–air surface are *yellow*.)

The experiments were conducted in a thermostat at 30°, the solutions being made up by mixing measured quantities of nitric acid (*d* 1·42) and water from two burettes, so that the total volume of liquid (*before* admixture) was 10 c.c. For convenience, the mixtures are designated by the volumetric percentage of nitric acid used in their preparation, a mixture prepared from 1·40 c.c. of water and 8·60 c.c. of nitric acid being referred to as 86% nitric acid.

The following results were obtained. Nitric acid of concentration 100—86% rendered iron passive, a distinct yellow colour being produced in 90—86% acid. When kept in these solutions, the passive iron dissolved so slowly that after 3 months very little dissolution had taken place.

The lowest concentration of nitric acid to passivate electrolytic iron at 30° was repeatedly determined as 86%. In 85·5% acid the iron disssolved with great vigour, and in 85·75% acid it dissolved quietly with slow evolution of bubbles.

Activation of Passive Iron by Whirling.—Pieces of iron foil 1 cm. × 2 cm. were pierced and suspended by a hook on the end of a glass rod, which could be rotated at a speed of 3000 r.p.m. in nitric acid. Iron whirled in nitric acid of any high concentration always imparted a distinct yellow colour to the solution after a short time, the more readily the greater the amount of water. The following is typical of many experiments: The iron, resting on the glass hook, was quickly passed through the liquid surface of 86% acid and was observed to be passive; it was then rotated at 3000 r.p.m., and no change occurred until after 30 seconds, whereupon the solution quite suddenly became deep yellow. After a further period of 60 seconds the iron had dissolved completely. Separate experiments showed that a similar piece of iron kept at rest in nitric acid of this concentration at 30° was completely dissolved after 8 days.

These experiments show beyond doubt that passive iron becomes active when rapidly whirled in nitric acid. The "induction period" of about 30 seconds is of exceptional interest, for it seems probable that this is the time taken to remove the protective oxide film, after which the dissolution proceeds apace.

Activation of Passive Iron by raising the Temperature.—Iron which has been made passive by concentrated nitric acid is well known to become suddenly active when the solution is heated. A study was made of this transition. The experiments were carried out in a thin-walled test-tube containing 10 c.c. of the nitric acid solution and a piece of iron foil measuring 1 cm. × 1 cm. A thermometer was suspended in the nitric acid. The whole was immersed in a large beaker of water, which was constantly stirred and heated at the rate

of 1° per minute by means of a small flame. The iron was thrown *into the nitric acid at 30°.*

In general, in the stronger solutions of nitric acid, the following *sequence of events was observed on raising the temperature.* At first the iron was passive and the solution almost colourless. At about 65° a faint yellow coloration appeared in the liquid, but suddenly at 75° slow evolution of small bubbles at the surface of the metal occurred: this transition was quite sharp. The rate of gas evolution increased slowly thereafter until at a higher temperature dissolution of the metal with almost explosive violence occurred very suddenly. In the following table are given the temperatures of these two sudden changes of iron in various concentrations of nitric acid:

Conc. of acid, %	100	99	98	95	90
1st temperature	*74·5°*	*74·5°*	*75·5°*	*74·5°*	*75·0°*
2nd "	86·5°	85·0°	83·0°	77·5°	75·0°

The table indicates that the first transition, corresponding with the first evolution of gas, takes place at a definite temperature of 74·5—75·5° independently of the concentration of the acid. The second transition temperature falls with increasing amounts of water in the mixture, until, for 90% acid, the metal passes from the passive state directly to the state of violent dissolution at 75°.

The results may be interpreted as follows: The first transition *marks the change from passive to active metal, due to dissolution* of the film by the nitric acid; the reaction is slow, however, because *the rate of dissolution of the film can only just keep pace with its* rate of re-formation as a result of the reaction. The second transition, or violent dissolution, denotes the complete disappearance of the film, and the temperature at which it occurs falls with decreasing concentration of nitric acid because of the greater solubility of ferric nitrate in weaker nitric acid solutions.

In order to test this hypothesis, the effect of nitric acid on ferric oxide was examined. Powdered ferric oxide was ignited in a silica crucible, cooled in a desiccator, and immediately placed in a test-*tube containing 10 c.c. of nitric acid (d 1·42). At the ordinary* temperature, no coloration was produced in the acid, and even on *standing for 24 hours at 30° only the faintest yellow was formed.* The rate of dissolution of ferric oxide in nitric acid under these conditions is therefore very roughly comparable with that of passive iron. When the temperature was slowly raised, as in the experiments with passive iron, the first faint yellow colour was produced at 68°; at 75°, the solution rapidly became deep yellow, and the thin deposits on the sides of the bottom of the tube vanished between 75° and 77°. The heating was continued up to 90° without change

other than a general deepening of the yellow colour. The total amount of ferric oxide dissolved was small. In an experiment carried out on freshly ignited ferric oxide in 90% nitric acid, the first faint yellow colour appeared at 64°, and the solution became deep yellow over the range 72—77°. It appears, therefore, that the temperature at which passive iron in nitric acid becomes active coincides with that at which the rate of dissolution of ferric oxide becomes appreciable.

Doubt is often expressed as to the existence of an oxide of iron capable of resisting the solvent action of concentrated acids, and statements are to be found in the literature to the effect that, apart from the inadequacy of known oxides of iron, it is necessary to assume that the oxide will be decomposed on heating in order to account for the activating effect. As shown above, the latter assumption is absolutely unnecessary, and the former objection is due to a misapprehension, for it is patent that freshly ignited ferric oxide dissolves in acids with extreme difficulty. Indeed, it is significant that the three metals which are most readily passivated (iron, chromium, aluminium) all give oxides which when freshly ignited are scarcely dissolved by acids.

Possibly the velocity of dissolution of the oxides is controlled by the existing degree of hydration of the particles. Thus, ordinary, powdered ferric oxide contains much adsorbed water and is much more readily soluble than the ignited material. If this "loosely combined" water is very great, as in a ferric hydroxide gel, the dissolution by nitric acid is immediate. These considerations also apply to the other oxides mentioned.

The reason for using freshly ignited ferric oxide in the experiments described above is that, since the protective film is formed under strictly dehydrating conditions on immersing iron in concentrated nitric acid, the water content of the ferric oxide is bound to be low and its properties will approximate to those of the ignited material.

It is also noteworthy that passive iron does slowly dissolve in concentrated nitric acid, the rate being controlled by the rate of dissolution of the oxide. This view is in complete accord with all the phenomena observed on raising the temperature.

Evidence that the Transition is not of Allotropic Nature.—In addition to the experiments described above, which directly support the oxide-film theory, negative evidence has been obtained which tends to show that the transition temperature does not mark anything in the nature of an allotropic change in the metal itself. Ordinary, active iron immediately becomes blackened when placed in silver nitrate solution, through deposition of metallic silver on its surface, whereas passive iron remains unchanged. If an allotropic change

from passive iron to active iron occurs at 75°, then a piece of passive iron, placed in silver nitrate solution, should cause deposition of silver as soon as the temperature reaches 75°. Actually, it was found that iron made passive by nitric acid can be heated in $0{\cdot}2N$-silver nitrate solution to boiling without any deposition of silver occurring. When the iron was kept for a long time in the silver nitrate solution, glistening crystals of silver were formed at isolated spots on its surface, probably representing discontinuities in the film.

Periodic Phenomena in the Activation of Passive Iron.—Periodic phenomena in the activation of aluminium and nickel passivated by anodic polarisation have been described by the author (J., 1926 2883) as occurring when the electrode is given equal opportunities o: being passive or active. A region of periodicity was observed whe1 any of the following three conditions were changed in the directio1 of increasing activity: (*a*) dilution of the reagent, (*b*) increase o temperature, (*c*) addition of an agent favouring activity.

Some support is lent to the supposition that electro-chemica passivity and that produced by purely chemical means are one an the same phenomenon, for with chemically passive iron simila periodic phenomena are observed when the passivating and activat ing influences are made nearly equal, by the same three method Herrschel (*Ann. Chim. Phys.*, 1833, **54**, 87) found that, in nitric aci intermediate in concentration between that required to passivat iron and that in which iron is rapidly dissolved, a piece of irc became alternately active and passive, gas being evolved in regul pulsations; but the present author, working at 30°, has not been ab to verify this.

Periodic phenomena were observed, however, in the experimen on the activation of passive iron by raising the temperature. every case, at the transition temperature (75°), evolution of g started in puffs which were at regular intervals in any one expe ment, but the intervals varied from 1 to 9 seconds in differe experiments. With rise of temperature the frequency of t periods increased. In addition to the visible changes, these perio are accompanied by an audible "pop," evidently caused by t suddenness of evolution of gas at the commencement of each peri The bright surface of the iron darkens during each rapid evoluti of gas, and when it is black the bubbles stop; as the surface bright again, evolution slowly increases, and the cycle is then repeat continuously.

The periodic formation of this visible dark film under th conditions offers additional support to the general explanation passivity which has been given; for, if a film is being formed un conditions such that it cannot become very protective, such a f

will grow and may readily reach visible thickness. At lower temperatures, where the conditions are not inimical to the permanence of a film, it is obvious that a film, once formed, will in virtue of its protective nature cease to grow. In such a case the film will be exceedingly thin.

Periodic phenomena have also been observed in the activation of passive iron by causing it to function as a cathode. This case is analogous to the addition of chlorine ions to anodically passivated nickel, the discharged hydrogen ions being the activating agent here. Heathcote (*Z. physikal. Chem.*, 1900, **35**, 210) noticed that an iron cathode in nitric acid becomes alternately active and passive. In the present investigation, the existence of periods in activation by this means was confirmed, but a detailed study of the effect of current density was precluded by the thinness of the iron foil (0·12 mm.).

Some experiments were also performed on the periodic passivation of iron by anodic polarisation in dilute sulphuric acid, and all the phenomena described in an earlier publication (J., 1926, 2878) were confirmed with the new specimen of iron.

Passivity of Other Metals at Low Temperatures.—Since the passivity of iron immersed in nitric acid is destroyed by heating to 75°, it appeared that other metals, not showing passivity at the ordinary temperature, might become passive towards concentrated nitric acid at lower temperatures.

Cobalt dissolved with great vigour in nitric acid of *d* 1·42 at the ordinary temperature, but became passive immediately at −11°. On raising the temperature slowly, the first bubbles appeared at +9°, and at 25° a sudden vigorous dissolution set in. Thus, the phenomena are precisely similar to those observed with iron at higher temperatures.

Nickel is said to be rendered passive by nitric acid (*d* 1·42) at the ordinary temperature. Of six samples (not analysed) of nickel examined under these conditions, four were rendered passive, and two were very rapidly dissolved. A specimen of the latter variety when added to nitric acid at −11° was immediately rendered passive. Again, the phenomena on warming resembled those of iron, for evolution of bubbles started suddenly at 30°, and at 72° violent dissolution set in.

Copper, when added to concentrated nitric acid at −11°, became covered with a visible, dark grey film and was inert, very little dissolution taking place in 2 days at the ordinary temperature. On warming, sudden violent dissolution occurred at 40°. Thus, the complete analogy with iron is established. The passivity of copper produced by this method is not so permanent as that of iron, for, if

the copper be removed from the nitric acid, washed with water, and replaced, it is found to be active, dissolving with vigour. The reason is that the film of cupric oxide is easily soluble in dilute nitric acid at the ordinary temperature, whilst ferric oxide is not. The fact that, in the case of copper, the oxide film has reached visible thickness is in itself an indication of its relatively poor protective value.

Zinc and magnesium were not rendered passive by nitric acid at −11°, but very slow evolution of gas occurred, suggesting that the metals were in the state between the two transition temperatures On warming, dissolution set in at +20° with such violence as tc project the acid from the test-tube.

Discussion.

Not only in the present research, but also from a general con sideration of the literature, there is a large amount of evidence whic suggests that passivity is a general property exhibited to variou extents by all metals under suitable conditions. It therefore seem illogical to limit the term, and with it the explanation, to a fe metals having peculiar electronic configurations which happen t exhibit the phenomenon particularly well at the ordinary ten perature.

The author has previously pointed out (J., 1926, 2885), from consideration of the current density–potential curves for anodes nickel and zinc, and from the existence of periodic phenomena, th there is no essential difference between the anodic polarisation these two metals. All the evidence appears to support the co clusion that passivity produced by anodic polarisation and purely chemical means is the same phenomenon, that it is the res of the formation of a film of oxidised material, and that it is exhibit to different degrees depending on the protective properties of t film *under the particular conditions prevailing.*

The Formation of Visible Films in Anodic Passivity.

When Evans succeeded in isolating a normally invisible film passive iron, difficulty was experienced in reconciling the fact w some observations made by the present author on the anodic pass ation of iron (*loc. cit.*). The experiments showed that immediat *before* passivation of the electrode a visible film * appeared on

* In the previous publication it was suggested that the observation of visible film was entirely new. Professor W. J. Müller, of Vienna, has poi out to me that he had observed its formation earlier (*Z. Elektrochem.*, 1 [illegible]

electrode and was thrown off as soon as evolution of oxygen started. This effect could be particularly well shown through the periodic phenomena when certain current densities were used. It was thus shown that the iron was without a visible film whilst passive, and acquired a visible film every time it became active. Clearly, the *visible film is not the protective film responsible for passivity.*

The facts can be reconciled completely by taking the following view of the nature of anodic polarisation. When an iron anode is dissolving in dilute sulphuric acid, there will be a certain critical current density above which sulphate ions are discharged more quickly than they can be replaced by diffusion. At this point, some hydroxyl ions will be discharged simultaneously. In addition, since hydrogen ions are repelled from the anode, the hydroxyl-ion concentration in the layer of liquid immediately contiguous to the anode will increase. The net result of these effects is the production of oxide or basic salt at the surface of the anode. Since sulphate ions are still being discharged, the film will not be continuous and thus, in virtue of its non-protective nature, will attain visible thickness. The relatively thick film will have the effect, however, of raising very greatly the effective current density at those areas of the electrode left uncovered. Consequently, at some isolated spots the discharge will consist mainly of hydroxyl ions, giving a perfectly continuous oxide film. Once this protective film has formed, it is immaterial whether sulphate ions or hydroxyl ions are discharged at its surface, for either will produce evolution of oxygen. Although the thin, invisible film cannot then grow in thickness, it will extend sideways, rapidly covering the whole electrode. At this stage, oxygen is evolved at the surface of the *invisible* film, causing the discontinuous *visible* film to be thrown off the electrode.

This view is supported by experiments which have been carried out on the influence of speed of rotation of the anode on periodic electrochemical passivity, and it is hoped to communicate the results shortly.

Meanwhile, an almost identical suggestion as to the rôle of the visible film has been published by W. J. Müller (*Monatsh.*, 1927, **48**, 61, 559; Müller and Noack, *ibid.*, p. 293), who differs from the present author, however, in supposing that the high effective current density caused by the partial covering of the electrode produces a change in the nature of the metal itself, to which passivity is due rather than to a protective film. Müller arrived at this view from a consideration of the time effect in passivation, and it is noteworthy that the same conclusions regarding the preliminary processes of electrochemical passivity have been reached by each of us from different points of view.

Summary.

Reproducible values for the lowest concentration of nitric acid necessary to passivate electrolytic iron can be obtained if care is taken to ensure that the iron passes rapidly through the liquid surface, which has an activating influence.

When passive iron is whirled at 3000 r.p.m. in nitric acid of this concentration it becomes active after a short induction period. This is shown to be in accordance with the oxide-film theory, the induction period representing the time for removal of the film, but is at variance with the theory advanced by Smits.

When passive iron in concentrated nitric acid is heated, dissolution of the metal begins at 74·5—75·5°, independently of the concentration of the acid.

Freshly ignited ferric oxide is not appreciably dissolved by concentrated nitric acid until this temperature is reached, and it is shown that this temperature does not represent an allotropic change in the metal.

Other metals can be passivated by nitric acid at lower temperatures; *e.g.*, at −11° copper becomes passive in concentrated nitric acid and is covered by a visible oxide film when in this state.

Periodic phenomena were observed in the activation of passive iron, both by increase of temperature and by cathodic polarisation. It is concluded that passivity produced by anodic polarisation and by purely chemical means is the same phenomenon, that it is the result of the formation of a film of oxidised material, and that it is exhibited to different degrees, depending on the protective properties of the film under the particular conditions prevailing.

A theory of the mechanism of anodic polarisation is advanced.

The author is much indebted to Mr. U. R. Evans, M.A., for the gift of electrolytic iron, and to the Research Fund Committee of the Chemical Society and the Trustees of the Dixon Fund of the University of London for grants which have assisted the research.

BEDFORD COLLEGE (UNIVERSITY OF LONDON),
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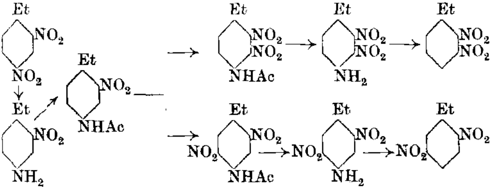
CXXVIII.—*Some Dinitroethylbenzenes.*

By OSCAR L. BRADY, JAMES N. E. DAY, and P. S. ALLAM.

THE present work is preliminary to an investigation of the nitration of *p*-ethyltoluene and similar compounds which is being undertaken with the view of ascertaining the relative ortho-directing influence of the various alkyl groups. The most convenient way of orienti

the substituents in the nitroethyltoluenes seems to consist in the oxidation of one alkyl group and the elimination of carbon dioxide from the resulting acid, leaving either nitrotoluenes or nitroethylbenzenes.

The early work on the latter compounds is not entirely satisfactory, but the investigations of Cline and Reid (*J. Amer. Chem. Soc.*, 1927, **49**, 3150), to whose paper reference may be made for an account of previous work, have removed much of the uncertainty regarding the properties of *o*- and *p*-nitroethylbenzene. Of the dinitro-compounds, only the 2 : 4-isomeride has been described and we have now prepared the 2 : 3-, 2 : 5-, 2 : 6-, and 3 : 5-dinitroethylbenzenes, the compounds which were likely to be of importance in connexion with the other investigation. 2 : 6- and 3 : 5-*Dinitroethylbenzenes* were prepared by the removal of the amino-group from 2 : 6-dinitro-4-aminoethylbenzene, prepared by the reduction of 2 : 4 : 6-trinitroethylbenzene, and from 3 : 5-dinitro-4-aminoethylbenzene, prepared by the nitration of *p*-acetamidoethylbenzene. The 2 : 3- and 2 : 5-*dinitroethylbenzenes* were prepared by the following series of reactions :



In the nitration of 2-nitro-4-acetamidoethylbenzene the 2 : 3-dinitro-compound is the chief product of the reaction in all cases, but a greater proportion of the 2 : 5-dinitro-compound is formed if a mixture of sulphuric and nitric acids is used instead of fuming nitric acid alone (compare Brady, Day, and Rolt, J., 1922, **121**, 527). The same behaviour has been observed in the case of 2-nitro-4-acetamidotoluene (compare Scott and Robinson, J., 1922, **121**, 844; Page and Heasman, J., 1923, **123**, 3235).

Experimental.

2 : 6-*Dinitroethylbenzene*.—Ammonium sulphide (29 c.c. of a 15% solution) was added slowly with frequent shaking to a solution of 2 : 4 : 6-trinitroethylbenzene (5 g.) (compare Schultz and Sander, *Ber.*, 1909, **42**, 2634) in boiling alcohol (30 c.c.), and the mixture

was then boiled for 30 minutes and filtered hot. On cooling, the filtrate deposited crystals (m. p. 160—165°). The solid residue was repeatedly extracted with boiling 2N-hydrochloric acid until the extract no longer gave a precipitate on the addition of ammonia. The extracts were neutralised with ammonia and the precipitate (m. p. 170°) obtained was crystallised, together with the above-mentioned crystals, from alcohol, giving 2 : 6-dinitro-4-aminoethylbenzene in golden-yellow needles, m. p. 175° (Found: N, 19·9. Calc.: N, 19·9%). Schultz and Sander (*loc. cit.*) give m. p. 110° for this compound.

A solution of 2 : 6-dinitro-4-aminoethylbenzene (2 g.) in a mixture of absolute alcohol (40 c.c.) and fuming sulphuric acid (10 c.c. containing 20% SO_3) was warmed on the water-bath, and dry sodium nitrite (6 g.) added in small quantities. After heating for 15 minutes, the pasty mass was diluted with water and distilled in steam. The volatile 2 : 6-*dinitroethylbenzene*, isolated by means of ether, crystallised from alcohol in colourless plates, m. p. 57·5° (Found: N, 14·7. $C_8H_8O_4N_2$ requires N, 14·3%). The compound was oxidised with boiling fuming nitric acid to 2 : 6-dinitrobenzoic acid, which was converted into the methyl ester; both acid and ester were compared with specimens prepared from 2 : 6-dinitrotoluene.

2-*Nitro*-4-*acetamidoethylbenzene*.—Ethylbenzene (21 g.) was added slowly to a mixture of nitric acid (28 c.c., d 1·42) and sulphuric acid (60 c.c., d 1·8), kept at 50—60°. The whole was heated on the water-bath for 30 minutes and cooled, and the liquid 2 : 4-dinitroethylbenzene was separated, washed with water, dissolved in boiling alcohol (10 g. in 30 c.c.), and treated with successive small portions of ammonium sulphide (70 c.c. of a 15% solution). After boiling for 30 minutes, the solution was filtered and cooled, the dark oil obtained was converted by concentrated hydrochloric acid into 2-nitro-4-aminoethylbenzene hydrochloride, and this was washed with ether to remove oily impurities and reconverted into the base by grinding with 2N-sodium hydroxide. The base (10 g.) was boiled for a few minutes with acetic anhydride (20 c.c.), and the cooled solution poured into water; the 2-nitro-4-acetamidoethylbenzene obtained, after crystallisation from benzene and light petroleum, melted at 111° (Found: N, 13·6. Calc.: N, 13·5%). Schultz and Sander (*loc. cit.*) give m. p. 100—101°, and Cline and Reid (*loc. cit.*), 110°.

Nitration of 2-*Nitro*-4-*acetamidoethylbenzene*.—The acetamido-compound (10 g.) was added slowly with stirring to a mixture of nitric acid (20 c.c., d 1·42) and sulphuric acid (20 c.c., d 1·8), kept below 30°. After 30 minutes, the solution was poured into a large

excess of water, and the precipitate was collected as rapidly as possible, washed free from acid with much ice-cold water, dried at room temperature, and dissolved in boiling glacial acetic acid (40 c.c.). The solid which separated on cooling, after one further crystallisation from glacial acetic acid, gave 2 : 3-*dinitro-4-acetamidoethylbenzene* in long, white needles, m. p. 143° (Found : N, 16·6. $C_{10}H_{11}O_5N_3$ requires N, 16·6%). The mother-liquor from the above was diluted with much water, the precipitate hydrolysed by heating on the water-bath for an hour with 45% sulphuric acid (30 c.c.), and the solution cooled and partly neutralised with 2*N*-sodium hydroxide. The precipitated mixture of amines (m. p. 87—92°) was crystallised from the minimum quantity of boiling alcohol. The crystals which separated (m. p. 120°), on further crystallisation from alcohol, gave 2 : 5-*dinitro-4-aminoethylbenzene* as red prisms, m. p. 125° (Found : N, 19·9. $C_8H_9O_4N_3$ requires N, 19·9%). A mixture of about equal quantities of this compound and 2 : 3-dinitro-4-aminoethylbenzene (m. p. 121·6°) melted at 87—93°.

2 : 3-*Dinitroethylbenzene*.—2 : 3-Dinitro-4-acetamidoethylbenzene was hydrolysed by heating on the water-bath with 45% sulphuric acid; 2 : 3-*dinitro-4-aminoethylbenzene* separated on cooling and after two crystallisations from dilute alcohol it was obtained in golden-yellow needles, m. p. 121·6° (Found : N, 20·1. $C_8H_9O_4N_3$ requires N, 19·9%). A solution of this compound (3 g.) in a mixture of absolute alcohol (50 c.c.) and fuming sulphuric acid (15 c.c. containing 20% SO_3) was warmed on the water-bath, and dry sodium nitrite added in small portions with stirring. On distillation with steam 2 : 3-*dinitroethylbenzene* passed over; it crystallised from dilute alcohol in white needles, m. p. 58·5° (Found : N, 14·4. $C_8H_8O_4N_2$ requires N, 14·3%). The compound (0·4 g.) was boiled under reflux with potassium dichromate (2 g.), sulphuric acid (10 c.c.), and water (10 c.c.), and from the cooled, diluted solution ether extracted 2 : 3-dinitrobenzoic acid, which was compared with a specimen prepared from 2 : 3-dinitrotoluene. The methyl ester was prepared by boiling the acid (0·5 g., obtained from either of the above sources) under reflux for 2 hours with methyl iodide and dry silver oxide (1 g.). The excess of methyl iodide was distilled off, and the ester extracted with hot methyl alcohol. On cooling, *methyl* 2 : 3-*dinitrobenzoate* separated in white plates, m. p. 134° in both cases (Found : N, 12·6. $C_8H_6O_6N_2$ requires N, 12·4%).

2 : 5-*Dinitroethylbenzene*, obtained, in the same way as the 2 : 3-compound, from 2 : 5-dinitro-4-aminoethylbenzene, separated from dilute alcohol or light petroleum in yellowish-white crystals, m. p. 59·5° (Found : N, 14·5. $C_8H_8O_4N_2$ requires N, 14·3%).

This compound was oxidised to 2 : 5-dinitrobenzoic acid, which was compared, and also its methyl ester, with specimens prepared from 2 : 5-dinitrotoluene.

3 : 5-*Dinitroethylbenzene*.—For the preparation of 3 : 5-dinitro-4-aminoethylbenzene the method of Paucksch was followed (*Ber.*, 1884, **17**, 769). Ethylbenzene was mononitrated, and the product reduced with tin and hydrochloric acid. Distillation in steam of the acid mixture removed a considerable quantity of unchanged nitro-compound, which was probably mainly *o*-nitroethylbenzene, since this compound is reduced with difficulty (Cline and Reid, *loc. cit.*). The crude amine (11 g. from 32 g. of ethylbenzene) obtained by distillation in steam of the solution after being made alkaline, was accordingly comparatively rich in *p*-aminoethylbenzene. Paucksch separated the two amines by crystallisation of their acetyl derivatives from water, but we were unable to achieve this satisfactorily. The mixture of amines (50 g.) was acetylated with acetic anhydride and a few drops of concentrated sulphuric acid, and the mixture poured into water. The oily solid produced, isolated by means of chloroform, became pasty after some days and was then pressed on a porous tile. The solid residue (20 g.) was added in small quantities to fuming nitric acid (200 c.c.) at $-6°$ to $-10°$. The solution, after being kept in the freezing mixture for 35 minutes, was poured into ice-water and the precipitate obtained was washed with water and crystallised from alcohol, giving 7 g. of 3 : 5-dinitro-4-acetamidoethylbenzene, m. p. 182—183° (Found: N, 16·7. Calc.: N, 16·6%). Hydrolysis of this compound with 50% sulphuric acid gave 3 : 5-dinitro-4-aminoethylbenzene, m. p. 135° (Found: N, 20·1. Calc.: N, 19·9%). Paucksch (*loc. cit.*) gives m. p.'s 182° and 135° for the acetyl and amino-compounds, respectively.

The amino-group in 3 : 5-dinitro-4-aminoethylbenzene (2·8 g.) was removed by diazotisation and treatment with boiling alcohol. By distillation in steam and crystallisation from light petroleum 3 : 5-*dinitroethylbenzene* (1·5 g.) was obtained as large, yellow plates, m. p. 41° (Found: N, 14·4. $C_8H_8O_4N_2$ requires N, 14·3%).

3 : 5-Dinitroethylbenzene (0·9 g.) was boiled under reflux for 3 hours with potassium dichromate (3·5 g.) and 50% sulphuric acid (30 c.c.). From the diluted solution, ether extracted 3 : 5-dinitrobenzoic acid, which, after crystallising from very dilute alcohol, was compared with an authentic specimen; the methyl esters also were compared.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, February 22nd*, 1928.]

CXXIX.—*Benzoic Esters and Electronic Affinities of Radicals. Part I.*

By Ahmad Zaki.

As a consequence of Robinson's ideas on orientation (*Chem. and Ind.*, 1925, **44**, 118, 563; J., 1926, 401, 1655), benzoic esters with alkyl or aryl radicals, repelling electrons more than the hydrogen they replaced in benzoic acid, should produce quantitatively, on nitration for instance, less *m*-compound than the free acid, whereas those attracting electrons should produce more of it. Nitration of benzoic esters, and estimation of the proportion of the *m*-isomerides afford a convenient auxiliary method for the estimation of the electron affinities of various groups, methyl benzoate being taken as the standard of reference.

The present paper records the results of an investigation of the alkyl benzoates. There is plenty of evidence to show that a methyl group has a smaller hold on electrons than a hydrogen atom (Lucas and Moyse, *J. Amer. Chem. Soc.*, 1925, **47**, 1459; Lucas, Simpson, and Carter, *ibid.*, p. 1462). It was accordingly anticipated (*a*) that as one ascended the series, normal alkyl benzoates would give, on nitration, a smaller percentage of the *m*-isomeride, (*b*) that aliphatic radicals with a branched chain would produce less *m*-compound than a normal-chain radical with the same number of carbon atoms, and (*c*) that the nearer the branching in the alkyl group to the benzoyl residue, the smaller would be the percentage of the *m*-isomeride.

Nitrations were first carried out at 25°, but with branched esters at that temperature nitric acid caused some decomposition with the formation of oxides of nitrogen. The nitrations were therefore carried out at 0°, with the following results.

	At 0°.		At 25°.	
Benzoate.	Meta.	Ortho + para.	Meta.	Ortho + para.
Methyl	72·6	27·4	69·7	30·3
Ethyl	69·9	30·1	66·3	33·7
n-Propyl	71·8	28·2	68·6	31·4
n-Butyl	67·9	32·1	65·1	34·9
n-Amyl	68·3	31·7		
n-Hexyl	63·7	36·3		
n-Heptyl	62·8	37·2		
n-Octyl	60·2	39·8		
n-Cetyl	52 (*ca.*)	48		
*iso*Propyl	64·1	35·9		
*iso*Butyl	69·4	30·6		
sec.-Butyl	65·2	34·8		
tert.-Butyl	59·4	40·6		
sec.-Octyl	59·4	40·6		

The results clearly agree with (*b*) and (*c*) above, but the anticipation (*a*) concerning the normal chains is evidently not verified

in the precise manner defined. The percentages of the *m*-isomeride obtained for the normal-chain benzoates are plotted in Fig. 1 as ordinates against the number of carbon atoms in the alkyl group as abscissæ.

The "general effect" due to a straight aliphatic saturated radical is the sum of the effects of all the carbon atoms it contains

FIG. 1.
Nitration of n-*alkyl benzoates.*

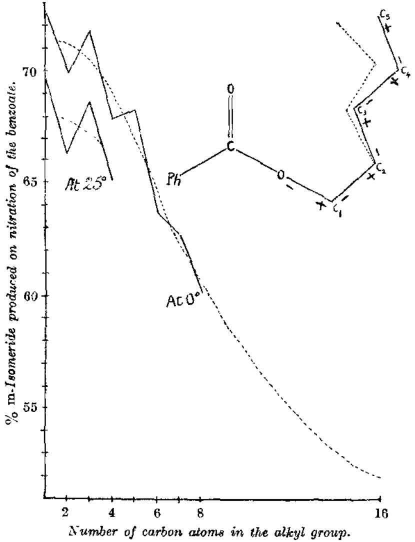


FIG. 2.

transmitted by electrostatic induction throughout the length of the chain (Allan, Oxford, Robinson, and Smith, J., 1926, 405; Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; Thomson, *Phil. Mag.*, 1923, **46**, 496; Lowry, *Trans. Faraday Soc.*, 1923, **18**, 293). According to the laws of electrostatic induction the further a carbon atom is removed from one end of the chain the less is its effect felt at that end. The curve anticipated for the normal alkyl benzoates as

plotted in Fig. 1 would on these assumptions be expected to slope downwards continuously with the lengthening of the chain, the slope diminishing as the series is ascended. Now the dotted line joining the middle points on the straight lines forming the zigzag curve in the figure, Stark's "form line" of the curve (*Z. anorg. Chem.*, 1921, **119**, 293), has a definite continuous downward slope indicating the fundamental truth of the above conceptions. According to Pauly (*Z. anorg. Chem.*, 1921, **119**, 271) and Müller and Shearer (J., 1923, **123**, 3156) the alcoholic carbon chain has a uniplanar zigzag configuration. Fig. 2 would therefore represent the configuration of the carbalkyloxy-group in the benzoic esters. Carbons numbered 3 and 5, including the hydrogen atoms they carry, would fall more within the field of influence of the carbonyl oxygen, whereby neutralisation of affinities through space occurs, than carbons 2 and 4. While affinities are being transmitted in the normal way through the bonds of the chain, neutralisation of affinities on the odd carbons might proceed to such a degree as to absorb the greater part of the former transmission. As the chain lengthens further, the additional carbon atoms, both in the even and in the odd positions, would be very nearly equally out of tbe sphere of influence of the carbonyl group and bond transmission alone would be felt, and alternation disappears.

Another factor which would make the above steric influence still more pronounced is the effect of distribution of the electric charges within the chain. According to Thomson (*loc. cit.*) the replacement of a hydrogen atom by a different atom or group is equivalent to the introduction of an electrostatic doublet whose magnitude and signs are dependent on the electronic nature of that atom or group. The orientation of the signs of the doublets introduced by the successive substitution of a methyl group for a hydrogen atom in forming the aliphatic chains is represented in Fig. 2. An alkyl group with an odd number of atoms would contain an even number of such doublets, each pair of which would attract one another, and the angle between the carbon linkings in each pair would be smaller than 109° 28′, which is the angle normally existing in the tetrahedral carbon atom. The zigzag structure would fold up closer together inwards towards the molecule, at the same time curving slightly round the carbonyl group (Fig. 2, dotted lines). By this means the neutralisation of charges through space becomes more effective at shorter distances and more odd carbon atoms are brought within the steric influence of the carbonyl oxygen, so that the influence is felt up to the *n*-heptyl ester. Alkyls with an even number of carbon atoms would on the other hand have an odd number of doublets, with the result that the end unpaired doublet, which occupies a sort of *trans*-

position with respect to the benzoyl part, would actually lessen the folding up of the structure, thus diminishing the steric effect and giving a clearer expression to the electronic repulsion as transmitted through the bonds.

Meerwein (*Annalen*, 1919, **419**, 121), studying quantitatively the pinacolin transformation of various tertiary glycols, has determined approximately the " affinity demands " of alkyl groups with straight and with branched chains. Taking a group of a great affinity demand to mean a group of greater hold on its electrons, it is found that his results accord exactly with the results of the present work and can be similarly explained.

After nitration of the esters and hydrolysis of the products as described in the experimental part, a method of determining the percentage of the *m*-isomeride in a mixture of the three nitrobenzoic acids based on Holleman's method (*Rec. trav. chim.*, 1899, **18**, 267; *Z. physikal. Chem.*, 1899, **31**, 79) was worked out.* It is more accurate than Holleman's method, which degree of accuracy was necessary in the case under consideration in order to detect small differences in the orienting powers of the groups. Owing to its general usefulness in orientation problems, a detailed account of it is given in the practical part.

EXPERIMENTAL.

Nitration of the Esters.—Nitric acid ($d^{14°}$ 1·517) free from oxides of nitrogen was freshly prepared for each nitration. The ester (3—4 g.) was introduced during $\frac{3}{4}$ hour into the nitric acid (12 c.c.) at 25° (thermostat) or 0° (ice). After remaining a further $\frac{3}{4}$ hour at the same temperature, the product was poured on 100 g. of crushed ice. The esters separating were extracted three times with 200 c.c. in all of ether that had been kept boiling for an hour over sodium and then distilled. The ethereal extract was freed from nitric acid by twenty washings with water (10 c.c.). The complete removal of acid was generally indicated by a small amount of a green colouring matter, a by-product in the nitration, passing into the washings. The aqueous washings were neutralised, and extracted with two quantities of 100 c.c. of ether. The ethereal extract was similarly washed several times with small quantities of water to remove a small amount of adhering colouring matter. On evaporation of the solvent from the combined ethereal extracts, an ester was obtained which was free from nitric acid and colouring matter. The aqueous washings left no appreciable residue when they were evaporated slowly to dryness on a steam-bath.

Hydrolysis of Nitration Products.—Acid hydrolysis at various

* Completed towards the end of March, 1927.

m-nitrobenzoic acid present in 25 c.c. of solution, and the whole amount of meta in the 175 c.c. was calculated. However, the presence of the *m*-nitrobenzoic acid in the analysis bottle causes more of the *o*-isomeride to dissolve than in the control bottle (Holleman, *loc. cit.*). To correct for this, a graph was plotted from results of analyses carried out on artificial mixtures in exactly the same way as described, the amounts of meta found being plotted against the amounts found in excess. The nitration products also contained slight excesses of acidity whose origin could not be traced with certainty. To correct for this, 2·000 g. of pure *m*-nitrobenzoic acid were added to each of the two bottles directly after the former titrations and the whole procedure was repeated once more. The differences in the titres represent foreign acidity and had to be allowed for.

It is essential to rotate the bottles for the time prescribed. When rotation lasted only 2 hours, unsaturated solutions were produced. This is in agreement with the experience of Paul (*Z. physikal. Chem.*, 1894, **14**, 110), that solutions of nitro- and similarly substituted benzoic acids required from 3 to 4 days for saturation. In order to draw clear solutions a small glass tube about 10 mm. in diameter and 15 mm. in length was drawn out at one end to simulate the narrow end of the standardised pipette, to which it was attached by a small piece of thin pressure tubing. Before the pipette was dipped in the solution, this inverted funnel was stuffed with three short layers of clean cotton-wool, each being more tightly packed than the one below it.

The baryta solution ($N/40$) was drawn by suction into a well-standardised 100 c.c. burette capable of holding more than is required by any one titration and with a scale reading accurately to 0·01 c.c. and a thin outlet delivering drops of not more than 0·03 c.c. This method of analysis should theoretically give results accurate within $\pm$ 0·3%. In practice, repeated determinations of the same mixtures, artificial and otherwise, under standard conditions gave results agreeing within $\pm$ 0·3%. Holleman's original method claims an accuracy of $\pm$ 1%.

Most of the esters are already described in the literature. sec.-*Butyl benzoate*. Equivalent quantities of benzoyl chloride and alcohol were heated under reflux for 4 hours, a little moist powdered calcium carbonate was added, and the heating continued for a further 4 hours. From 16 g. of alcohol, 30 g. of ester, b. p. 148—151°/50 mm., were obtained (yield, 75%).

n-*Amyl benzoate*. The alcohol was heated with benzoyl chloride for 5 hours. B. p. 138—139°/15 mm. (Found : C, 75·1; H, 8·3. Calc. : *C*, 75·0; *H*, 8·3%). The ester was prepared by Blaise and Picard (*Ann. Chim. Phys.*, 1912, **25**, 261), but not analysed.

tert.-*Amyl benzoate.* Into a boiling solution of sodium (3·4 g.) in dry *tert.*-amyl alcohol (50 g.), a mixture of newly distilled methyl benzoate (20 g.) and *tert.*-amyl alcohol (26 g.) was introduced in drops during an hour. After boiling for another hour, the product was worked up in the usual manner and fractionated at 22 mm. The ester required was collected between 127° and 128° (yield, 17 g.; 60%) (Found: C, 75·2; H, 8·5. Calc.: C, 75·0; H, 8·3%). The nitration of this ester, however, proved a failure owing to decomposition.

n-*Hexyl benzoate.* Equivalent quantities of benzoyl chloride and the alcohol were boiled very gently for 5 hours. The yield of crude product exceeded 70%. B. p. 200—202°/100 mm.

n-*Heptyl benzoate.* This was prepared in the same way as the hexyl ester. B. p. 216—217°/100 mm. (Found: C, 76·5; H, 9·3. Calc.: C, 76·4; H, 9·1%).

sec.-*Octyl benzoate.* Same preparation as in the two previous esters with similar good yield. B. p. 218—219°/100 mm.

Cetyl benzoate. After the preparation of the ester (Becker, *Annalen*, 1857, **102**, 221) it was purified by distillation at 9 mm.; it came over steadily between 300° and 301° without decomposition. It was, however, difficult to separate all the cetyl alcohol from the mixture of nitrobenzoic acids obtained, and the result of analysis can only be taken as a very approximate one.

The author wishes to thank Professor R. Robinson and Dr. O. L. Brady for their kind interest in this work, and the authorities of University College for facilities for carrying it out.

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UNIVERSITY COLLEGE, LONDON. [*Received, January 28th*, 1928.]

CXXX.—*The Parachor and Chemical Constitution. Part IX. Boron Compounds.*

By JOSEPH JOHN ETRIDGE and SAMUEL SUGDEN.

MOST of the atomic parachors so far studied are those of elements in Groups IV to VII of the periodic table. The parachor of boron is therefore of special interest since its value will show whether atomic parachors, like atomic volumes in the solid state, pass through a minimum value at carbon. For this reason we have measured the surface tension and density of methyl and ethyl borates; the parachors obtained from these data are recorded in Table I together with that of boron trichloride calculated from the recent measurements of Mills and Robinson (J., 1927, 1823). The column headed $\Sigma[P]$ gives the sum of the atomic constants except

TABLE I.

	$[P]$ obs.	$\Sigma [P]$.	Boron.
Methyl borate	243·7	228·3	15·4
Ethyl borate	363·1	345·3	17·8
Boron trichloride	178·8	162·9	15·9
		Mean	16·4

that of boron, which is obtained by subtracting $\Sigma[P]$ from $[P]$ obs. The three values obtained are in satisfactory agreement in view of the fact that they are found from the difference of two much larger quantities, any errors of measurement being magnified considerably.

The mean value, 16·4, shows clearly that atomic parachors pass through a sharp minimum at carbon. An approximate valne for lithium is given by the measurements of Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1), and it is hoped shortly to complete this series by measurements on compounds of beryllium.

Li.	Be.	B.	C.	O.	F.
ca. 50	—	16·4	4·8	20·0	25·7

In the course of this work it was found that methyl alcohol and methyl borate form a mixture of maximum vapour pressure which boils at 55° and contains 30% of the ester.

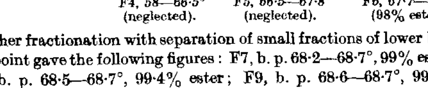
EXPERIMENTAL.

The chief methods which have been employed for the preparation of boric esters are : (i) the action of boron trichloride on the alcohol (Ebelman and Bouquet, *Annalen*, 1846, **60**, 251); (ii) the action of boric anhydride on the alcohol nnder pressure (Schiff, *Annalen*, 1867, Snppl. 5, 158; Copaux, *Compt. rend.*, 1898, **127**, 719); (iii) the distillation of anhydrous borax with the alkyl potassium sulphate (Rose, J., 1856, 574; Frankland, *Annalen*, 1862, **124** 132); (iv) the action of the alcohol on the mixed anhydride of boric and acetic acids (Pictet and Geleznov, *Ber.*, 1900, **33**, 2221). The fourth method is recommended by Beilstein, but we made several unsuccessful attempts to prepare the esters in this way. The crude product of the action of methyl alcohol on the mixed anhydride was found to be a ternary mixture of methyl alcohol b. p. 65°, methyl borate, b. p. 69°, and methyl acetate, b. p. 57° from which we were unable to ohtain the pure ester by repeated fractionation. The separation was complicated by the occurrence of the constant-boiling mixture of methyl alcohol and methyl borate described below. The method is also of little value for the preparation of the ethyl ester, b. p. 117°, which cannot be separated by distillation from the acetic acid, b. p. 118°, set free when the ester is formed. Pictet and Geleznov do not mention these diffi-

culties and it is probable that the methyl and ethyl esters which they describe were not pure substances.

The method by which the pure esters were finally obtained was a modification of that of Schiff and Copaux (*locc. cit.*). At first excess of boric anhydride was used, but this appeared to give a product (probably metaboric ester) which decomposed during distillation.

Methyl borate. 70 G. (1 mol.) of boric anhydride and 100 g. (3 mols. + 5%) of methyl alcohol, dried over aluminium amalgam, were placed in a pressure bottle which was closed and shaken vigorously to prevent caking of the anhydride. The bottle was heated at 120° in an oil-bath for 12 hours, and the contents on distillation gave a 68% yield of crude ester, b. p. 55—65°. The crude product was then fractionated and the fractions were analysed by decomposing a weighed amount with water and titrating the liberated boric acid with alkali in the presence of glycerol, bromophenol-blue being used as indicator. The crude ester contained 70% of Me_3BO_3; it was placed over freshly ignited calcium chloride for 24 hours to remove some methyl alcohol and then fractionated through a 2-foot column filled with glass beads. It soon became evident that methyl alcohol and the borate form a mixture of constant boiling point and maximum vapour pressure. This was isolated and found to contain only 30% of the ester and to boil at 55°. Small amounts of the alcohol can therefore be separated from the ester by distillation. The course of the separation is shown by the scheme below.



Further fractionation with separation of small fractions of lower boiling point gave the following figures: F7, b. p. 68·2—68·7°, 99% ester; F8, b. p. 68·5—68·7°, 99·4% ester; F9, b. p. 68·6—68·7°, 99·6% ester; and F10, b. p. 68·7°/765 mm., 99·9% ester. The physical constants given in the literature for this ester vary considerably:

Boiling point.	Density at 0°.
72° (Ebelman).	0·940 (Schiff).
65° (Schiff).	0·919 (Gasselin).
55—56° (Gasselin).	0·955 (Ebelman).
68·7°/765 mm. (present authors).	0·9547 (present authors).

It is evident that Gasselin's product was the constant-boiling mixture and not the pure ester.

Ethyl borate. This substance was prepared in a similar manner and was more easily purified. The crude ester was obtained in 76% yield, and fractionated after treatment with calcium chloride. A constant-boiling mixture was not observed, and a few distillations gave a product, b. p. 117·2°/740 mm., which was found to contain 99·9% ester. The constants quoted in the literature for this ester are in much better agreement:

Boiling point.	Density at 0°.
120° (Schiff).	0·887 (Schiff).
119·5° (Copaux).	0·886 (Ghira).
117·2°/740 mm. (present authors).	0·8864 (present authors).

The surface tensions of these esters were measured by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). As the esters are very readily hydrolysed, a long tube coated internally with phosphoric oxide was used to dry the air entering the bubbler. The density of the liquid, D, was determined in sealed tubes by means of carefully calibrated floats. The vapour density, d, was calculated by the method described in an earlier paper (J., 1925, **127**, 1540). The parachor was obtained by the formula $P = M\gamma^{1/4}/(D - d)$, where M is the molecular weight and γ the surface tension in dynes/cm.

Methyl borate, $C_3H_9O_3B$, $M = 104·0$. Densities determined: $D_{4°}^{24·3°}$ 0·9205; $D_{4°}^{40·2°}$ 0·8981; whence $D_{4°}^{t°} = 0·9547—0·00141t$.

t	15°	33·5°	52°	
γ	22·66	20·50	18·00	
$D - d$	0·9330	0·9062	0·8792	
Parachor	243·2	244·2	243·6	Mean 243·7

Ethyl borate, $C_6H_{15}O_3B$, $M = 146·0$. Densities determined: $D_{4°}^{10°}$ 0·8746; $D_{4°}^{28°}$ 0·8546; $D_{4°}^{52°}$ 0·8264; whence $D_{4°}^{t°} = 0·8864 - 0·00115t$.

t	15°	35·5°	50°	64°	
γ	21·80	19·52	18·02	16·60	
$D - d$	0·8691	0·8452	0·8282	0·8118	
Parachor	363·1	363·0	363·2	363·1	Mean 363·1

One of us (S. S.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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CXXXI.—*A Further Case of the Spontaneous Resolution of Externally Compensated Mixtures.*

By LEONARD ANDERSON and DOUGLAS WILLIAM HILL.

As long ago as 1852 Pasteur (*Ann. Chim.*, **34**, 46) observed that a concentrated solution of inactive ammonium hydrogen malate first deposited, on evaporation, crystals which resembled the active salt in form. This observation was confirmed by van 't Hoff and Dawson (*Ber.*, 1898, **31**, 528), who showed the crystals to consist of a mixture of 3 parts of ammonium hydrogen *l*-malate with 1 part of the *d*-salt, thereby indicating that a partial resolution of the inactive malate had occurred. Malic acid has also been resolved by crystallisation of inactive ammonium molybdomalate (Darmois and Périn, *Compt. rend.*, 1923, **176**, 391). Examples of the spontaneous resolution of sodium ammonium racemate have been recorded by Gernez (*Compt. rend.*, 1866, **63**, 843), Ostromisslensky (*Ber.*, 1908, **41**, 3035), and Kipping and Pope (J., 1909, **95**, 103). Inactive lactic acid has been resolved by Purdie (J., 1893, **63**, 1143), who inoculated concentrated aqueous solutions of its zinc ammonium salt with crystals of the active salt. Werner (*Ber.*, 1914, **47**, 2171) has shown that inactive co-ordination compounds of cobalt and chromium also may be resolved into their active antipodes by similarly inoculating super-saturated aqueous solutions.

The most complete investigation of the effect of inoculation was carried out by Ostromisslensky (*loc. cit.*), who showed that on seeding a *dl*-mixture with an isomorphous substance, one or other antipode is exclusively precipitated. For this purpose he used, besides active tartrates and malates, *l*-asparagine, which caused crystallisation of pure sodium ammonium *d*-tartrate. He also showed that the inoculating crystals need not be optically active or even possess an asymmetric atom.

Such well-defined results, however, have not been obtained by every investigator. For instance, Darmois and Périn (*loc. cit.*) record that inoculation of solutions with a crystal of known sign gives very variable results. Kipping and Pope (*loc. cit.*) too, who at first attributed the crystallisation of sodium ammonium *d*-tartrate from the racemate to the presence of undetected *d*-tartaric acid in the original racemic acid, afterwards drew the conclusion that the presence of dust in the atmosphere was sufficient to cause deposition of either one or other of the isomerides.

In view of the problems which these observations raise, it was considered of interest to put on record a new instance of this phenomenon, namely, the spontaneous resolution of atropine sulphate.

Atropine is prepared commercially by racemisation of the naturally occurring *l*-hyoscyamine and the commercial product is frequently faintly *l*-rotatory. On crystallising this racemised atropine sulphate from absolute alcohol several times, hyoscyamine sulphate of $[\alpha]_D \pm$ *ca.* 14° was obtained regularly, and on further crystallisation of collected crops of this specific rotatory power a hyoscyamine sulphate of $[\alpha]_D \pm$ *ca.* 20° was produced. When the resolution was carried out in a works laboratory in which *l*-hyoscyamine had been racemised, the crop was almost invariably lævorotatory (Table II), but when it was carried out in another laboratory in which the first experiment had shown a predominance of *d*-sulphate in the product of several crystallisations the proportion of crops containing an excess of *l*-hyoscyamine sulphate was considerably decreased (Table III). It is essential to employ a well-dried alcohol for the resolution, and in most cases we have used 99·5% alcohol. In some cases in which the alcohol was not specially dried, little resolution took place (Table IV).

In order to determine whether this resolution of atropine sulphate was due to traces of optically active material present in it or not, a quantity of partly synthetic atropine sulphate of certain inactivity was prepared from synthetic tropic acid and this behaved precisely similarly to atropine sulphate prepared by racemisation of *l*-hyoscyamine, for after five crystallisations from absolute alcohol it gave a product having $[\alpha]_D + 14°$. The results therefore support Kipping and Pope's view that these cases of spontaneous resolution are due, not to undetected traces of an optically active variety, but to inoculation from the atmosphere.

Attempts were also made to effect a separation of atropine sulphate by using a mixture of ethyl acetate and methyl alcohol as solvent, but the original material was unaltered after several crystallisations. Unsuccessful attempts were also made to resolve homatropine sulphate with 99·5% and absolute alcohol as solvents; atropine oxalate, with water and 80% alcohol; atropine alkaloid, with benzene; and tropic acid, with 99·5% alcohol. The specificity of the phenomenon appears to indicate a particular solubility relationship. The final product is different from the original, being much less hygroscopic and less soluble in alcohol. It crystallises well without scratching from five to six times its weight of solvent and does not exhibit the same tendency to form super-saturated solutions —a peculiarity which appears to be common to all the cases of spontaneous resolution so far examined.

EXPERIMENTAL.

Crystallisation of Atropine Sulphate from Alcohol.—Atropine ulphate previously dried at 100° was crystallised from twice its eight of alcohol, and the crystals obtained were collected by means f a pump and immediately recrystallised without drying. Crystal-sation, which was on all occasions sluggish, was assisted by cooling ice-water and vigorous scratching of the super-saturated solution ith a glass rod. After several crystallisations this became unneces-ary, since the later crops were less soluble and crystallised well on anding in a desiccator. The mother-liquor from each crystallis-tion was precipitated separately with either acetone or ether, the nal crop of crystals and the precipitates being dried at 100° and eir rotatory powers in 10% aqueous solution determined.

Experiment A.—Atropine sulphate (25 g.) (m. p. 189—190° and $[\alpha]_D - 0{\cdot}25°$) was crystallised as described above six times from bsolute alcohol. A final crop (2·1 g.) was obtained with m. p. 201° nd $[\alpha]_D + 15{\cdot}43°$, corresponding to 59% excess of hyoscyamine lphate.

Table I gives details of the crops from the mother-liquors.

TABLE I.

Cryst.	Wt. of alcohol used (g.).	Wt. of ppt. from mother-liquor (g.).	M. p. of ppt.	$[\alpha]_D$ of ppt.
A 1	50	8·9	192°	−3·93°
A 2	40	3·9	193	−4·79
A 3	35	3·8	190	+2·50
A 4	30	1·7	192	+1·46
A 5	20	1·2	193	+7·82
A 6	10	0·4	193	—

The results of a number of similar experiments carried out under nditions in which the presence of inoculating particles of the vo-salt was to be expected are in Table II and of experiments rried out in a separate laboratory in Table III.

The irregular results shown in Table II are due to the presence of rying small amounts of moisture in the alcohol used. In the periments shown in Table III, only absolute alcohol was employed. he effect of using commercial absolute alcohol which had not been ecially dried is shown in Table IV.

Fractional Crystallisation of Atropine Sulphate.—Atropine sulphate 00 g.) previously dried at 100° was dissolved in warm 99·5% alcohol 50 g.) and crystallised under a bell-jar. The fraction (a 1) tained was recrystallised from 700 g. of alcohol, and the crystallised rtion (a 2) again filtered off. Meanwhile, the mother-liquor I L 1) from the first crystallisation was precipitated by the addi-n of ether, and this precipitate (b) was crystallised from the

TABLE II.

Exp.	Wt. of atropine sulphate used (g.).	Initial $[\alpha]_D$.	No. of crystns.	$[\alpha]_D$ of final product.	Percentag excess of *l*-hyoscyami sulphate.
B	25	−3·2°	4	−14·73°	57
C	25	−3·2	5	−14·76	57
D	25	−0·45	6	− 4·60	18
E	25	−0·46	8	−11·50	45
F	50	−0·46	8	−19·50	75
G *	25	−0·40	8	+ 9·25	36
H *	25	−0·80	10	− 8·30	32
I	100	−0·30	10	− 4·75	19
J	25	−4·75	5	−13·40	52
K	25	−0·45	5	−16·85	65
L	300	0·00	12	−16·00	61
M	110	0·00	10	− 9·75	39

* All the experiments were carried out with atropine sulphate of Boo manufacture with the exception of G and H, in which Boehringer's a Merck's products respectively were used for comparison.

TABLE III.

Exp.	Wt. of atropine sulphate used (*g.*).	Initial $[\alpha]_D$.	No. of *crystns.*	$[\alpha]_D$ of final *product.*	Wt. of final product (*g.*).	Percentag excess of hyoscyami *sulphate.*
N	25	0·00°	5	+14·70°	1·5	57 *d*-
O	25	0·00	7	−13·67	6·2	53 *l*-
P *	20	0·00	5	+14·04	1·4	54 *d*-
A	25	−0·25	6	+15·43	2·1	59 *d*-

* Synthetic atropine sulphate.

Experiment A is included here to make clear the increased proportion experiments yielding the dextro-salt.

TABLE IV.

Illustrating the effect of moisture.

Exp.	Wt. of atropine sulphate used (g.).	Initial $[\alpha]_D$.	No. of crystns.	$[\alpha]_D$ of final product.
R	60	−0·46°	8	−1·7°
S	30	−0·46	5	−0·7
T	25	−0·45	5	+4·9

filtrate of the second crystallisation, yielding a fresh fraction (b and a fresh mother-liquor (M L 2). This process of crystallising ea crop from the preceding filtrate was continued until eight fractio had been obtained. These were dried and their weights and speci rotatory powers are given in Table V. (Determinations of the spe fic rotatory power were made at different points during the cryst lisation, and since fraction b 6 did not crystallise from the mothe liquor of a 7, the value obtained for b 4 is included to indicate t direction of the rotation).

Crystallisation of Synthetic Atropine Sulphate.—The atropi sulphate was obtained by converting synthetic tropic acid, pr

TABLE V.

Fraction.	M. p.	Wt. (g.).	$[\alpha]_D$.	Percentage of hyoscyamine sulphate.
a 8	200°	18	−13·82°	53 *l*-
(b 4)	—	—	(+10·74)	(41 *d*-)
c 6	200	19	−13·17	51 *l*-
d 5	200	21	+11·48	45 *d*-
e 4	201	35	+11·24	44 *d*-
f 3	200	10	−11·69	46 *l*-
g 2	200	21	−10·35	40 *l*-
h 1	198	15	+ 9·80	38 *d*-
i	191	10	+ 2·86	12 *d*-

ared by Müller's method (*Ber.*, 1918, **51**, 252), into acetyltropyl hloride, condensing this with tropine hydrochloride, and hydrolysing he acetylatropine produced as described by Wolffenstein and lamlock (*Ber.*, 1908, **41**, 723). The atropine was converted into ulphate and showed no optical activity in a 10% aqueous solution. fter five crystallisations from absolute alcohol, the final crop had ı. p. 198° and $[\alpha]_D$ + 14·04° (see Table III, Exp. P).

Further Separation of Active Fractions.—(a) The lævorotatory actions from a number of experiments were collected and dried nd 25 g. were crystallised from absolute alcohol in the usual ıanner. After six crystallisations, the first three each from 150 g. f alcohol and the last three each from 100 g. of alcohol, the final rystallised product (8 g.) had m. p. 206° and $[\alpha]_D$ − 20·58°.

(b) Similarly, 25 g. of the collected dextrorotatory fractions were rystallised each six times from 100 g. of absolute alcohol. The final rop (8·5 g.) had m. p. 207° and $[\alpha]_D$ + 20·12°.

The two rotations recorded correspond to an excess of hyoscy-nine sulphate amounting to 79% *l*- and 77% *d*-, respectively.

Specific Rotatory Power of the Free Alkaloid.—The most active action obtained in (a) above, having $[\alpha]_D$ − 20·58°, was dissolved ı water, and the alkaloid precipitated by sodium hydroxide. The recipitate was well washed with water and dried in a desiccator ver sulphuric acid: its specific rotatory power in 10% solution in 9% alcohol was $[\alpha]_D$ − 13·17°.

The same procedure was adopted also in experiment K, the final ystallised product, $[\alpha]_D$ − 16·85°, and the crop from the first other-liquor, $[\alpha]_D$ + 7·60°, yielding atropine alkaloid with $[\alpha]_D$ − 2·10° and + 5·6°, respectively.

The authors wish to thank Dr. F. L. Pyman, F.R.S., for his dvice and Mr. W. H. Sims for carrying out many of the crystallis-tions and determinations of rotatory power.

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CXXXII.—*The Chlorination of Anilides. Part III.* N-*Chlorination and* C-*Chlorination as Simultaneous Side Reactions.*

By KENNEDY JOSEPH PREVITÉ ORTON, FREDERICK GEORGE SOPER, and GWYN WILLIAMS.

THE conversion of chloroamines into nuclear-substituted anilides, thought at one time to be a typical intramolecular rearrangement, has been shown (Orton and W. J. Jones, P., 1909, **25**, 196, 233, 305; *Brit. Assoc. Reps.*, 1910, 85) to proceed thus : *

$$\mathrm{Ar{\cdot}NHAc + Cl_2} \begin{cases} \rightarrow \mathrm{Cl{\cdot}Ar{\cdot}NHAc + HCl} & (a) \\ \rightleftharpoons \mathrm{Ar{\cdot}NClAc + HCl} & (b) \end{cases} \quad . \quad (\mathrm{I})$$

The evidence may be briefly summarised, since it appears to have been largely overlooked or disregarded by some authors, and the older view, that chloroamines are necessary intermediates in the nuclear chlorination of anilides, still finds expression (Francis, *Chem. Rev.*, 1926, **3**, 274; Francis, Hill, and Johnston, *J. Amer. Chem. Soc.*, 1925, **47**, 2230; Francis, *ibid.*, 1926, **48**, 1637; Mathews and Williamson, *ibid.*, 1923, **45**, 2574; Porter and Wilbur, *ibid.*, 1927, **49**, 2145; de Lange, *Rec. trav. chim.*, 1926, **45**, 19; van Alphen, *ibid.*, 1927, **46**, 287, 799). The facts are :

(1) Hydrochloric acid is the agent which brings about the " transformation " (Armstrong, J., 1900, **77**, 1047) and is, further, the only substance which so acts (Orton and Jones, *loc. cit.*).

(2) In solution, an equilibrium is formed, represented by equation (I*b*) (Orton and Jones, *loc. cit.*; J., 1909, **95**, 1456).

(3) The same proportions of *o*- and *p*-chloroacetanilides are obtained whether the starting materials are acetanilide and chlorine or *N*-chloroacetanilide and hydrochloric acid (Orton and Bradfield, J., 1927, 986; this vol., p. 351). This holds for all three solvents examined.

(4) *In water and in aqueous acetic acid of less than 65% strength*, the rate of " transformation " of *N*-chloroacetanilide is less than the rate of nuclear chlorination of acetanilide (Orton and Jones, *loc. cit.*). In water, the rate of " transformation " is equal to the calculated

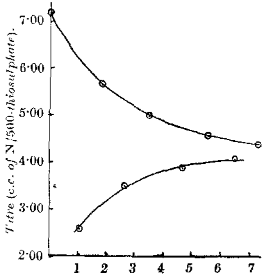
* Compare Orton, *Brit. Assoc. Reps.*, 1912, 117 : " Whether a true intramolecular change is possible under certain conditions has not yet been discovered, but it must not be supposed that the possibility is excluded."

In addition to the references cited, see *Brit. Assoc. Reps.*, 1911, 94; 1912, *116; 1913, 136; 1914, 105; 1915, 82;* also Orton and King, J., *1911*, **99**, 1185. 1369.

rate of formation of chlorine from *N*-chloroacetanilide and hydrochloric acid (Soper, *J. Physical Chem.*, 1927, **31**, 1192).

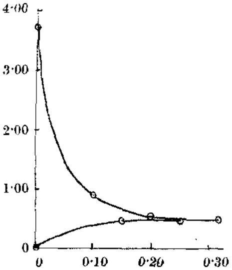
Subsequent work has called for no revision of the main conclusion reached in 1909. Further confirmation has now been obtained by actual measurement of the velocities of the two individnal reactions, *N*-chlorination and *C*-chlorination, in 40% acetic acid. Moreover, by the use of a new method of analysis, it is shown that, in the *reaction between chlorine and anilides, the ratio of the amounts of* chloroamine and chloroanilide formed at a given moment is independent of the time. Wegscheider's test (*Z. physikal. Chem.*, 1899, **30**, 593) is thus satisfied, and chloroamine formation and nuclear chlorination are therefore simultaneous.

FIG. 1.



Expt. 27.—p-*Chloroacetanilide.*

FIG. 2.



Expt. 93.—*Aceto*-p-*toluidide.*

The position of the equilibrium (I*b*) depends greatly on the composition of the medium; in glacial acetic acid, chloroamine is indetectable, but as the medium is diluted with water, the equilibrium is displaced until, in 50% acetic acid, it lies entirely on the chloroamine side (Orton and Jones, *loc. cit.*). The position of equilibrium in 40% acetic acid thus allows chloroamine formation to he treated as though it were an irreversible reaction. 2 : 4-Dinitroacetanilide is an exception in that the equilibrium mixture in this medium contains a considerable amount of free chlorine.

The aspiration method for the analysis of mixtures containing both chloroamine and free chlorine (Orton and Jones, *loc. cit.*) has been replaced by one in which the chlorine is removed by a suitable reagent, leaving the chloroamine for titration. Acetanilide, aromatic ethers, and phenols have been used as absorbers of chlorine,

p-cresol being especially suitable, for it reacts instantaneously with chlorine but has no appreciable reaction on the chloroamines under investigation, and, in acid solution, does not react with iodine.

The reaction is followed by transferring known volumes of the (naturally, already acid) reacting mixture *alternately* to (*a*) aqueous potassium iodide, which gives the chlorine + chloroamine concentrations, and (*b*) aqueous *p*-cresol, which removes chlorine, whereupon the chloroamine is determined by addition of potassium iodide and titration. The titres (in c.c. of $N/500$-thiosulphate) are plotted against time (in minutes) in Figs. 1 and 2. The lower section of the curve in the diagram corresponds to (*b*) and represents the course of the *N*-chlorination, whilst the upper branch is formed from the titres of (*a*), and its fall shows the extent of *C*-chlorination These curves are used to calculate k_N and k_C from the equations

$$k_N + k_C = \frac{2 \cdot 303}{t(a - b)} \log \left[\frac{b}{a} \cdot \frac{a - (x + y)}{b - (x + y)}\right]; \quad k_N/k_C = y/x,$$

where k_N and k_C are the velocity coefficients of *N*- and *C*-chlorination respectively, and y and x are the concentrations (in the same units of chloroamine and chloroanilide formed. Owing to the great speed of the reactions, it is not possible to determine experimentally a large number of points on the curves, but we have found that the effect of a slight error in drawing the curves is negligible. The results obtained for seven anilides are given in Table I.

TABLE I.

Temp., 18° (± 0·02°). Medium, 40% acetic acid.

	k_N.	k_C.
o-Chloroacetanilide	286	27·5
m-Chloroacetanilide	172	3,140
p-Chloroacetanilide	115	135
p-Bromoacetanilide	123	116
Aceto-*o*-toluidide	140	1,390
Aceto-*p*-toluidide	2,540	18,500
Acetanilide	96	11,000

The constancy of k_N/k_C for each anilide throughout the reaction is shown by Table II and by the examples of experimental figures given below.

EXPERIMENTAL.

Materials.—The anilides were specially prepared for these experiments and recrystallised at least twice from alcohol or dilute acetic acid. Acetanilide was sublimed.

The reaction medium (40% acetic acid by weight, *i.e.*, 6·90*M* acetic acid at room temperature) was made up by mixing glacial acetic acid, stabilised to chlorine by the method of Orton and Brad

field (J., 1924, **125**, 960; 1927, 983), with water purified by distillation successively from chromic acid and from baryta in a modified form of the apparatus of Moseley and Myers (*J. Amer. Chem. Soc.*, 1918, **40**, 1409). Velocity measurements made with independently prepared specimens of anilide and different preparations of medium gave results which were indistinguishable.

Chlorine. "Cylinder" chlorine was washed with water and passed into 40% acetic acid. Measurements with chlorine solutions are liable to error through chemical instability of the solvent and/or volatility of the solute. Solutions prepared as above were sufficiently stable for one hour at 18° and were used as the source of chlorine for the reactions.

p-Cresol. B.D.H. or Kahlbaum specimens were redistilled and used in saturated aqueous solution (0·185*M*).

Stability of p-*Cresol to Chloroamines in Dilute Acetic Acid Medium.*—A saturated aqueous solution of *p*-cresol was left in contact with solutions (in 40% acetic acid) of two chloroamines with widely different hydrolysis constants (in 20% acetic acid, Soper and Smith, this vol., p. 138). In neither instance was there any change in the titre obtained after adding potassium iodide solution. 0·01*M*-*N*-Chloroacetanilide (hydrolysis constant, $6·7 \times 10^{-7}$) had an initial titre of 19·40 c.c. of 1·0*N*/100-thiosulphate, and after standing for 30 mins. with 10 c.c. of *p*-cresol solution, a similar quantity had a titre of 19·38 ± 0·02 c.c.: 0·005*M*-*N*-Chloro-*m*-nitroacetanilide (hydrolysis constant, 99×10^{-7}) had an initial titre of 10·57 c.c. of 0·96*N*/100-thiosulphate, and after standing with 20 c.c. of the *p*-cresol solution for 70 mins., the titre was 10·58 c.c.

Velocity Measurements.

The initial concentration of chlorine was usually of the order 0·0005—0·001*M*, and of the anilide 0·001—0·003*M*. The anilide was present in excess in order to avoid complications due to the formation of chloroamines of the primary products of nuclear chlorination (compare Soper, *loc. cit.*), and the reactions were carried out in the presence of hydrochloric acid to suppress the hydrolysis of chlorine (Jakowkin, *Z. physikal. Chem.*, 1899, **29**, 613). In 40% acetic acid medium, 0·01*M*-hydrochloric acid was sufficient for this purpose, the rate of reaction being unaffected by alteration of the hydrochloric acid concentration over the range 0·01—0·10*M*. Higher concentrations of acid caused marked changes, not only in the speed of *N*-chlorination (as was to be expected from equation I), but also in the rate of *C*-chlorination; *e.g.*, for *p*-chloroacetanilide:

Conc. of HCl	0·01—0·10	0·50	1·0	3·5
k_C	135 (k_N = 115)	108	68·3	30·9

A 5·5M-standard solution of hydrogen chloride in 40% acetic acid was used for making up the required concentration of hydrochloric acid in the reaction mixture. In the final experiments, 0·2 c.c. of this solution was added to the anilide solution in a 100 c.c. standard flask. The chlorine solution was prepared as already described. When both solutions had attained the temperature of the thermostat, the reaction was started by running chlorine solution into the anilide from a 5 c.c. pipette, graduated to 0·05 c.c., to fill up to the 100 c.c. mark (about 3 c.c. were needed). For estimation, the first 1 c.c. of the chlorine solution was run directly into aqueous potassium iodide. Control experiments showed that an accurate determination of the initial chlorine concentration was obtained in this way.

The composition of the reaction mixture was then determined by transferring portions at noted times to a series of flasks containing alternately potassium iodide solution and *p*-cresol solution. After addition of potassium iodide to each cresol flask, the iodine was titrated (titration error, ± 0·02 c.c. N/500-thiosulphate). Oxidation of hydriodic acid and consequent masking of the end-point was prevented (*a*) by passing a stream of nitrogen through the solutions in the flasks before the experiment for a few minutes and again during titration (Soper, J., 1924, **125**, 1899), or (*b*) by reducing the acidity by the addition of freshly prepared sodium acetate solution. Method (*b*), which was used occasionally, is only applicable in the absence of cresol.

Times were reckoned from the moment of entry of the first extract into the arresting agent and not from the time of mixing the reactants and were measured by a stop-watch graduated to 0·2 sec.; the timing error was estimated at ± 1 sec. (0·017 min.). With reactions of the speed measured, escape of chlorine into the atmosphere during pipetting is negligible (compare, in particular, the experiments of Soper, *J. Physical Chem.*, 1927, **31**, 1195). The following experiment is given as an example.

Expt. 27. *p*-Chloroacetanilide = 0·002424M. Chlorine = 0·000932M. HCl = 0·10M. Thiosulphate = 1·005N/500.

Time (min.) ...	0	1·00	1·75	2·53	3·40	4·50	5·40	6·30	7·10
Titre (c.c.) ...	7·21	2·58	5·67	3·51	5·00	3·89	4·59	4·10	4·39

From the curves constructed with these figures (Fig. 1), we have :

Time.	KI titre.	:NCl titre.	Diff.	% Change.	$k_N + k_O$.	k_N/k_O.
0	6·45	2·44	4·01	67		0·861
1·25	5·53	3·26	2·27	76	253	0·869
2·25	5·12	3·61	1·51	84	248	0·868
4·00	4·69	3·95	0·74	92	251	0·861
5·25	4·51	4·07	0·44	95	255	0·854
					Mean 252	0·863

The reproducibility is shown by the following figures for *p*-chloro-ıcetanilide.

Expt.	16.	19.	20.	27.	18.	Mean.
$k_N + k_C$	245	247	255	252		250 ± 1·5%
k_N/k_C	0·821	0·859	0·866	0·863	0·840	0·850 ± 1·7%

Table II gives the values for the ratio (chloroamine formed)/ chloroanilide formed)—*i.e.*, k_N/k_C—for four other anilides. Over he range accessible to analysis, the ratio is satisfactorily constant. lthough the reactions are so fast that it is difficult to examine their arly stages, it may be inferred that k_N/k_C is constant throughout, ince values calculated from the *initial* concentration of chlorine gree with those obtained by taking a point in the analysed portion f the reaction as starting point. Moreover, special experiments vith *p*-chloroacetanilide over the range 10—30% change have iven a value of k_N/k_C in agreement with the above.

TABLE II.

o-*Chloroacetanilide.*

Time.	% Change.	k_N/k_C.
0	49	(6·16)
2·00	85	10·35
3·10	90	10·52
4·00	93	10·50
5·00	96	10·45
6·50	98	10·50
	Mean	10·46
	Mean of 3 expts.	10·40

m-*Chloroacetanilide.*

Time.	% Change.	k_N/k_C.
0	64	0·0543
0·100	71	0·0547
0·183	76	0·0552
0·333	84	0·0553
0·500	89	0·0555
0·700	92	0·0574
0·900	94	0·0597
	Mean	0·0560
	Mean of 5 expts.	0·0548

p-*Bromoacetanilide.*

Time.	% Change.	k_N/k_C.
0	20	1·10
0·90	40	1·01
2·00	58	1·02
2·95	68	1·07
5·00	84	1·10
7·20	91	1·08
	Mean	1·06
	Mean of 3 expts.	1·06

Aceto-o-*toluidide.*

Time.	% Change.	k_N/k_C.
0	52	0·102
0·250	69	0·109
0·350	74	0·112
0·550	81	0·115
0·850	87	0·115
	Mean	0·111
	Mean of 2 expts.	0·102

Measurement of the Speed of the Faster Reactions.—When the action speeds were very fast (acetanilide, aceto-*o*- and -*p*-toluidides, -chloroacetanilide), the experimental procedure was modified as llows. The reactants were mixed very quickly by pouring rapidly large volume (*e.g.*, 196 c.c.) of anilide solution into a small volume .*g.*, 4 c.c.) of chlorine solution in a beaker flask, both solutions eing at 18°. The reaction mixture was at once poured alternately ito the potassium iodide and cresol flasks which had previously een weighed with corks. Finally, 5 c.c. of potassium iodide soluon were run into each of the flasks containing the cresol. The asks were corked and re-weighed and the iodine was titrated.

Knowing the density of the reaction medium (determined as 1·050 at 18°) and the weight of 5 c.c. of potassium iodide solution added to each cresol flask, the concentrations of chlorine and chloroamine could be calculated. The volume of the reaction mixture was usually 200 c.c., and about 40 g. were poured into each flask. The times at which the reaction mixture was tipped out were memorised.

Control experiments proved that (*a*) reaction between chloroamine and hydrochloric acid in the cresol flasks pending the addition of potassium iodide and (*b*) oxidation of hydriodic acid during the second weighing could both be neglected, and further, (*c*) that *volatility of the chlorine is not a disturbing factor.*

Although there seems, at first sight, a possibility of considerable timing errors, this method gives satisfactory results for reactions whose time of half-completion is as little as 10 seconds. As illustration, the results obtained for aceto-*p*-toluidide are given. In this case, owing to the great speed of the reaction, the time of mixing had to be taken as zero.

Expt. 93. Aceto-*p*-toluidide = 0·001120*M*. Chlorine = 0·000259*M*. HCl = 0·01*M*. Thiosulphate = 1·39*N*/500. Vol. of reaction mixture = 200 c.c.

Time (min.)	0	0·100	0·150	0·200	0·250	0·317
Wt. (g.)		30·96	48·88	31·40	37·31	53·09
Titre (c.c.)		1·32	1·09	0·79	0·87	1·26
Calc. titre for 20 c.c....	3·73	0·90	0·47	0·53	0·49	0·50

From the curves constructed with these titres (Fig. 2), we find :

Time.	KI titre.	:NCl titre.	Diff.	% Change.	$k_N + k_C$.	k_N/k_C.
0	3·73	0	3·73			
0·080	1·11	0·34	0·77	79	20,000	0·130
0·100	0·90	0·39	0·51	86	20,500	0·138
0·150	0·64	0·47	0·17	95	21,900	0·152
				Mean	20,800	0·140

Expt. 94. Aceto-*p*-toluidide = 0·000956*M*. Chlorine = 0·000264*M*. HCl = 0·01*M*. Thiosulphate = 0·991*N*/500. Vol. of reaction mixture = 250 c.c.

Time (min.) ...	0	0·083	0·133	0·167	0·217	0·250	0·325
Wt. (g.)		32·52	58·04	51·88	28·95	39·21	31·10
Titre (c.c.)		2·41	1·56	2·40	0·55	1·52	1·03
Calc. titre for 40 c.c.	10·66	3·12	1·13	1·95	0·80	1·63	1·39

From the curves :

Time.	KI titre.	:NCl titre.	Diff.	% Change.	$k_N + k_C$.	k_N/k_C.
0	10·66	0	10·66			
0·083	3·12	0·87	2·25	79	22,500	0·116
0·133	2·19	1·13	1·06	89	22,000	0·133
0·167	1·95	1·22	0·73	93	20,600	0·140
0·210	1·73	1·31	0·42	96	20,100	0·147
				Mean	21,300	0·134

The other results obtained by this method were :

Acetanilide (3 expts.), $k_C = 11{,}000 \pm 1\cdot8\%$; *m*-chloroacetanilide (3 expts.), $k_N + k_C = 3310 \pm 3\cdot5\%$; aceto-*o*-toluidide (2 expts.), $k_N + k_C = 1530$, 1530.

Determination of k_N/k_C *for Acetanilide.*—With this substance, the rate of *N*-chlorination ($k_N = 96$) is small in comparison with the rate of *C*-chlorination ($k_C = 11{,}000$) and cannot be followed in a velocity experiment. The ratio k_N/k_C is determined by using higher concentrations of acetanilide and chlorine and measuring the residual titre when reaction is complete. A large excess of acetanilide must be used and precautions are necessary in order to minimise the formation of the chloroamines of *o*- and *p*-chloroacetanilides which would give too high a value for k_N/k_C (Soper, *loc. cit.*). No concordant results could be obtained until the following procedure had been developed.

0·2 C.c. of a 5·5*M*-solution of hydrogen chloride in 40% acetic acid was added to 50 c.c. of the acetanilide solution. After being adjusted to 18°, a standard solution of hypochlorous acid * in 40% acetic acid was run in, drop by drop, from a burette graduated to 0·05 c.c., to the solution, which was stirred mechanically. After the addition, potassium iodide was added and the iodine was titrated in an atmosphere of nitrogen.

Experiments were made with two different specimens of hypochlorous acid, (A) prepared by the action of chlorine on mercuric oxide, and (B) by the action of carbon dioxide on bleaching powder solution; seven experiments gave for the ratio k_N/k_C (*i.e.*, residual titre/fall of titre) the value $0\cdot00873 \pm 1\cdot6\%$. The chlorine concentration was of the order 0·002—0·008*M*, and the proportion of acetanilide to chlorine was varied from 16/1 up to 52/1.

One of us (G. W.) wishes to express his thanks to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant. We desire also to thank the Royal Society for a grant which has partially defrayed the cost of this investigation.

* The interaction between hypochlorous acid and acetanilide to form the *N*-chloro-derivative has been measured in these laboratories and found to be slow (unpublished research).

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CXXXIII.—*The Chlorination of Anilides. Part IV The Significance of Velocity Measurements in Relation to the Problem of Benzene Substitution.*

By Alan Edwin Bradfield and Brynmor Jones.

The quantitative study of the chlorination of anilides (Orton an Bradfield, J., 1927, 986; Bradfield, this vol., p. 351) has no been extended to include certain phenolic ethers,* in which th para-position is occupied by halogen, nitro-, or carboxy-group The uncertainty in the interpretation of velocity measuremen when two positions in the benzene nucleus are attacked is avoid by a study of compounds of this type, since chlorine enters only the ortho-position to the group ·OR, and, further, the very hi rates of reaction of the unsubstituted ethers are retarded by *p*-substituent of this type, and become conveniently measurable 20°. The velocity coefficients now described, except for some the values in Table I, relate to the "99% acetic acid" mediu (*i.e.*, containing 1 c.c. of water per 100 c.c. of reaction mixtur previously employed (Orton and Bradfield, *loc. cit.*) and we calculated from the ordinary expressions for bimolecular reactio (time in minutes, concentrations in g.-mols. per litre).

So far as it has yet been examined, the velocity of chlorinati of phenolic ethers increases rapidly with increasing water conte of the medium, the increase for an alteration from 1% to 2% water being almost as great as for a rise of temperature of 1 (Table IA). The effect of varying the concentration of hydrochlor acid is shown in Table IB.

TABLE I.

Chlorination of *p*-chloroanisole at 20°.

Conc. of *p*-chloroanisole = 0·0075 g.-mol./litre.
„ chlorine = 0·0075 g.-mol./litre.

A. Effect of water in medium.			B. Effect of HCl. 99% Acetic aci	
C.c. of H_2O per 100 c.c.	Mol. proportions of HCl.	*k*.	Mol. proportions of HCl.	*k*.
1	5	1·32	1·2	1·22
2	5	2·20	1·5	1·26
1	8	1·41	5·0	1·32
1·13	8	1·48	8·0	1·41

It is seen from Tables II and III that the velocity coefficients a slightly altered by a change in the relative concentrations of eth and chlorine. So far as possible, standard conditions have be employed throughout, in order that the results may be comparabl

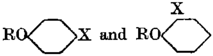
* For a preliminary investigation, which was interrupted by the war, s Orton and D. C. Jones, *Brit. Assoc. Reps.*, 1915, 82.

hough the low reactivity of the p-nitro-ethers necessitated working at much higher concentrations than were required for the other substances. It is difficult to estimate the absolute order of accuracy of the measurements, but with any given substance consistently reproducible results could be obtained within about 2%. Each of the values quoted is the mean of several determinations.

Evidence was sought for a possible displacement of the carboxyl group by chlorine in the derivatives of p-hydroxybenzoic acid investigated (compare Francis and Hill, *J. Amer. Chem. Soc.*, 1924, **46**, 2498). Examination of the individual values of k for the chlorination of several compounds of this type showed that when the molecular proportion of ether and chlorine was 1 : 1, there was a slight upward drift as the reaction progressed, which was, however, within experimental error. This would be accounted for by the occurrence, to a small extent, of the successive reactions: $RO{\cdot}C_6H_4{\cdot}CO_2H \xrightarrow{Cl_2} RO{\cdot}C_6H_4Cl \xrightarrow{Cl_2} RO{\cdot}C_6H_3Cl_2$. The disturbance is almost entirely eliminated when the initial ratios are 3 : 1 or 10 : 1, and a satisfactorily constant coefficient is obtained. The agreement between the values at the two different concentrations shows that the results at the lowest concentration (1 : 1) are not seriously vitiated.

TABLE II.

Velocity coefficients for the chlorination of substances of the types



in 99% acetic acid, at 20°.

Conc. of chlorine throughout = 0·0075 g.-mol./litre (1 mol.).
,, hydrochloric acid throughout = 0·0375 g.-mol./litre (5 mols.).

Conc. of ether		0·0075	0·0225	0·075
Mol. propn. of ether		1	3	10
		Velocity coefficients.		
Group X.	Group R.			
Cl (p-)	CH_3-	1·323	1·226	—
,,	C_2H_5-	—	2·443	—
,,	n-C_3H_7-	—	2·756	—
,,	*iso*-C_3H_7-	—	5·377	—
,,	n-C_4H_9-	—	2·723	—
,,	$C_6H_5{\cdot}CH_2$-	0·8783	0·8371	0·8054
,,	p-$C_6H_4Cl{\cdot}CH_2$-	—	0·4834	—
,,	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$-	—	0·1742	0·1828
,,	m-$NO_2{\cdot}C_6H_4{\cdot}CH_2$-	—	0·2104	0·2068
Cl (o-)	CH_3-	—	4·441	—
,,	C_2H_5-	—	8·873	—
,,	p-$NO_2{\cdot}C_6H_4{\cdot}CH_2$-	—	0·6417	0·6586
CO_2H (p-)	CH_3-	0·4624	0·4440	0·4389
,,	C_2H_5-	0·9084	0·8774	0·8712
,,	n-C_3H_7-	—	0·9563	—
,,	*iso*-C_3H_7-	2·053	1·975	—
,,	n-C_4H_9-	1·038	0·9633	—
,,	$C_6H_5{\cdot}CH_2$-	0·3232	0·3143	0·3002

TABLE III.

Chlorination of substances RO NO_2 at 20°.

Conc. of chlorine = 0·02 g.-mol./litre (1 mol. proportion).
,, HCl = 0·05 ,, (2·5 mol. proportions).
,, ether = 0·20 ,, (10 mol. proportions).

Group R.	CH_3-	C_2H_5-	*n*-C_3H_7-
$k \times 10^6$	2993	5983	6612

Discussion of Results.

The Introduction of a Second Substituent into a Monosubstituted Benzene Derivative.—The success of the application of the concept of kinetic activation to bimolecular gaseous reactions (Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, 1926) warrants an examination of its applicability to the problem of benzene substitution, which, it has long been recognised, is essentially a problem of relative reaction rates. By analogy with the expression for simple gaseous bimolecular reactions, the equation $k = PSZe^{-E/RT}$ may be set up, where $E = E_A + E_B$ represents the energy of activation corresponding to substitution at a particular carbon atom, $Z/2$ is the number of collisions between the reacting molecules in unit time, and S is a factor (depending on the shape of the molecule) representing the probability that the molecules are oriented in a manner favourable to reaction at the moment of collision. The idea that the rate of substitution at a given point in the benzene nucleus depends on a "phase" condition of the nucleus is involved in several theories of benzene substitution, and the P term denotes the probability that the phase condition of the molecules admits of reaction.

Since, in a monosubstituted benzene derivative, there are two ortho- and two meta-positions, and one para-,

$$k_o = 2PSZe^{-E_o/RT},\ k_m = 2PSZe^{-E_m/RT},\ \text{and}\ k_p = PSZe^{-E_p/RT}.$$

In the case of a reaction yielding only *o*- and *p*-derivatives, $k_o/k_p = r_1$ represents the ratio of the total *o*-compound formed to the total *p*-compound, at a temperature T_1. If, provisionally, it be assumed that the P and S factors are identical for the two positions, $k_o/k_p = 2e^{(E_p-E_o)/RT}$, and for two temperatures, T_1 and T_2,

$$2{\cdot}303 \log_{10} (r_1/2) = (E_p - E_o)/RT_1 \quad . \quad . \quad . \quad . \quad (1)$$

and $$2{\cdot}303 \log_{10} (r_2/2) = (E_p - E_o)/RT_2$$

whence $$\log_{10} (r_1/2)/\log_{10} (r_2/2) = T_2/T_1 \quad . \quad . \quad . \quad . \quad (2)$$

Hence, if r_1 be known at a temperature T_1, r_2 for a temperature T_2 may be evaluated. In a similar manner, the ratio *o*- : *m*- : *p*-, for a reaction yielding all three isomerides, at any one temperature, can be calculated from the values at another temperature.

These relations would not be expected to hold (1) for the sulphonation of aromatic compounds, owing to the migration of the $\cdot SO_3H$ group at higher temperatures, (2) for the substitution reactions of basic substances in acid media, (3) for the nitration of phenol (which appears to be a complicated reaction: compare Martinsen, *Z. physikal. Chem.*, 1904, **50**, 385; Arnall, J., 1923, **123**, 3111), or for the *chlorination of toluene, which follows an unusual course* (Holleman, "Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910). Table IV has been constructed by taking all the data, not excluded by the above considerations, which are quoted by Holleman (*op. cit.*), mainly from investigations in his own laboratories, on the effect of temperature on the proportions of the isomerides formed by further substitution in mono- and di-substituted benzenes, and from the value of r_1 at one temperature, calculating r_2 at a higher temperature, and comparing the results with the observed values. In all cases, the alteration in the proportions of the isomerides is in the right direction, and of the correct order of magnitude. Although the accuracy of the experimental work of Holleman and his collaborators is probably unsurpassed by other workers in this field, the *exact* agreement, in some cases, between the observed and calculated values must of course be regarded as fortuitous. Nevertheless, the good general agreement appears to support the assumptions involved, and suggests the adoption of the working hypothesis that the primary factor deciding the proportions of the isomerides formed in aromatic substitution reactions is the energy of activation corresponding to the different positions available, and not the phase relationships of the molecule. The question of the retention of a "phase factor," which is the same for all the simultaneous reactions by which the isomerides are formed, remains untouched.

TABLE IV.

Isomerides formed in nitration of	Temp.	Proportions.	Temp.	Proportions. Found.	Proportions. Calc.
C_6H_5Cl (*o*- *p*-)	—30°	26·9 : 73·1	0°	30·1 : 69·9	30·7 : 69·3
C_6H_5Br (*o*- : *p*-)	—30	34·4 : 65·6	0	37·6 : 62·1	37·8 : 62·2
C_6H_5I (*o*- : *p*-) *	—30	39·1 : 60·9	0	41·1 : 58·7	42·1 : 57·9
$C_6H_5\cdot NO_2$ in HNO_3 (*o*- : *m*-) †	0	6·4 : 93·2	30	8·3 : 91·0	8·2 : 91·1
$C_6H_5\cdot NO_2$ in H_2SO_4 (*o*- : *m*-) †	0	4·8 : 93·5	40	6·8 : 91·8	6·9 : 91·7
$C_6H_5\cdot CH_3$ (o- : m- : p-)	*—30*	*55·6 : 2·7 : 41·7*	*0*	*56·0 : 3·1 : 40·9*	*56·0 : 3·8 : 40·2*
$C_6H_5\cdot CH_3$ (*o*- : *m*- : *p*-)	—30	55·6 : 2·7 : 41·7	60	57·5 : 4·0 : 38·5	56·1 : 6·2 : 37·7
$C_6H_5\cdot CH_3$ (*o*- : *m*- : *p*-)	0	56·0 : 3·1 : 40·9	60	57·5 : 4·0 : 38·5	56·3 : 5·3 : 38·4
$C_6H_5\cdot CO_2H$ (*o*- : *m*- : *p*-)	—30	14·4 : 85·0 : 0·6	30	22·3 : 76·5 : 1·2	19·2 : 79·7 : 1·1
$C_6H_5\cdot CO_2Me$ (*o*- : *m*- : *p*-)	—30	23·6 : 74·4 : 2·0	30	25·7 : 69·8 : 4·5	27·5 : 69·2 : 3·3
$C_6H_5\cdot CO_2Et$ (*o*- : *m*- : *p*-)	—40	25·5 : 73·2 : 1·3	30	27·7 : 66·4 : 5·9	30·0 : 67·5 : 2·5
o-$C_6H_4Cl_2$ (1,2,3 : 1,2,5)	—30	5·2 : 94·8	0	7·2 : 92·8	7·0 : 93·0
m-$C_6H_4Cl_2$ (1,3,2 : 1,3,4)	—30	*2·6 : 97·4*	0	*3·8 : 96·2*	*3·8 : 96·2*
o-$C_6H_4Cl\cdot CO_2H$ (1,2,3 : 1,2,5)	—30	14·0 : 86·0	0	16·0 : 84·0	16·6 : 83·4
m-$C_6H_4Cl\cdot CO_2H$ (1,3,2 : 1,3,6)	—30	7·0 : 93·0	0	8·0 : 92·0	9·1 : 90·9
o-$C_6H_4Br\cdot CO_2H$ (1,2,3 : 1,2,5)	—30	17·1 : 82·9	0	19·7 : 80·3	19·7 : 80·3
m-$C_6H_4Br\cdot CO_2H$ (1,3,2 : 1,3,6)	—30	11·0 : 89·0	0	13·0 : 87·0	13·5 : 86·5

* Holleman, *Rec. trav. chim.*, 1913, **32**, 134.

† A small, variable amount of the *p*-isomeride has not been taken into account.

The Introduction of a Third Substituent into a Disubstituted Benzene Derivative.—The problem of calculating the resultant directive effects of two groups, present together in the nucleus, from a knowledge of their effects when present separately, can only be approached in a tentative manner. In a simple case, such as the nitration of *o*-dichlorobenzene, the nitro-group enters position 6 or 4, *o*- or *p*-, respectively, to one chlorine atom, and *m*- to the other. A simple hypothesis would be that the energies of activation of positions 6 and 4 correspond to the energies of activation of the *o*- and *p*-positions in chlorobenzene, increased (or diminished) by some quantity C due to the presence of a second chlorine atom in the nucleus. For chlorobenzene, we have equation (1) above, and for dichlorobenzene we have a similar relation qualified by the circumstance that there are now two positions ortho and two positions para to a chlorine atom :

$$2{\cdot}303 \log k'_o/k'_p = [(E_p + C) - (E_o + C)]/RT \quad . \quad . \quad (3)$$

and from (1) and (3),

$$k'_o/k'_p = k_o/2k_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

That this relation will not hold, in general, may be seen from the table given by Holleman (*op. cit.*, p. 483), who used (4) as an empirical expression. Further, it is easily shown that analogous assumptions to those employed above are implicit in Francis's attempt to deal with the cumulative effect of groups (*J. Amer. Chem. Soc.*, 1926, **48**, 1631), which again does not always lead to satisfactory results.

Nevertheless, the velocity measurements now recorded provide some justification for this method of treatment for a series of closely related compounds. Neglecting the small variations in collision numbers due to differences in molecular weight, for the series of compounds p-X·C_6H_4·OR, where X = ·Cl, ·CO_2H, etc., and R = Me, Et, etc., and symbolising the increment in the energy of activation, due to X_1 and X_2, of the carbon atom ortho to the group OR by E_1 and E_2, we have :

$$*k^{OMe}_{p\text{-}Cl} = 2Ze^{-(E_o+E_1)/RT}, \quad k^{OEt}_{p\text{-}Cl} = 2Ze^{-(E_o'+E_1)/RT}$$

$$k^{OMe}_{p\text{-}CO_2H} = 2Ze^{-(E_o+E_2)/RT}, \quad k^{OEt}_{p\text{-}CO_2H} = 2Ze^{-(E_o'+E_2)/RT},$$

whence $$k^{OEt}_{p\text{-}Cl}/k^{OMe}_{p\text{-}Cl} = e^{(E_o-E_o')/RT} = k^{OEt}_{p\text{-}CO_2H}/k^{OMe}_{p\text{-}CO_2H},$$

or, in general, $$k^{OR}_{X_1}/k^{OMe}_{X_1} = k^{OR}_{X_2}/k^{OMe}_{X_2}.$$

That is, the relative directive powers of two groups ·OR_1 and ·OR_2, as measured by the ratio of the velocity coefficients, should be

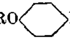
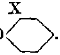
* $k^{OR}_{p\text{-}X}$ represents the velocity coefficient for the chlorination of p-X·C_6H_4·OR.

independent of the nature of the group X. Table V, in which the ratios k_X^{OR}/k_X^{OMe} (multiplied by 100 for convenience) for the ethers are tabulated in the four series in which X = *p*-Cl, *p*-CO_2H, *p*-NO_2, and *o*-Cl, shows that the present experiments support this conclusion.

For purposes of comparison, the relative effects of the *p*-chloro-, *p*-carboxy-, and *p*-nitro-groups, and of *o*- and *p*-chloro-groups, as measured by ratios of the type $k_{X_1}^{OR_1}/k_{X_2}^{OR_1}$, are given in Tables VI and VII. *Finally, from Table VIII, it may be seen that, although the* velocity coefficients vary slightly with the initial molar proportions of the reactants, by taking the ratios for a pair of substances from the two values in the same vertical column of Table II, a constant is obtained which is independent of the actual initial molar proportions.

From the point of view of modern theories of benzene substitution, considerable interest attaches to these measurements of relative directing power, but further discussion is reserved, pending the completion in these laboratories of certain allied investigations.

TABLE V.

Relative directive effects of the groups ·OR in compounds of the types ROX and RO. Values of $100k_X^{OR}/k_X^{OMe}$.

R =	Me.	Et.	Pr^a.	Pr$^\beta$.	Bu.	CH_2Ph.	$CH_2\cdot C_6H_4\cdot NO_2$ (*p*-).
X = *p*-CO_2H	100	198	215	444	221	70	—
p-NO_2	100	200	221	—	—	—	—
p-Cl	100	190	225	439	222	67	14·2
o-Cl	*100*	*199*	—	—	—	—	14·4

	Me.	$CH_2\cdot C_6H_4Cl$ (*p*-).	$CH_2\cdot C_6H_4\cdot NO_2$ (*m*-).
p-Cl	100	39·4	17·2

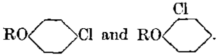
TABLE VI.

Relative directive effects of the groups ·CO_2H, ·Cl, and ·NO_2 in compounds of the type RO X. Values of $100k_X^{OR}/k_{p\text{-}CO_2H}^{OR}$.

	X = ·CO_2H.	·Cl.	·NO_2.
R = Me	100	276	0·674
Et	100	278	0·682
Pr^a	100	288	0·691
Pr$^\beta$	100	272	
Bu^a	100	283	
CH_2Ph	100	269	

TABLE VII.

Relative effects of *o*- and *p*-Cl in compounds of the types



R =	Me.	Et.	CH_2Ph.
$100k^{OR}_{o\text{-}Cl}/k^{OR}_{p\text{-}Cl}$ =	362	363	364

TABLE VIII.

Effect of relative concentrations of ether and chlorine on the ratios $100k^{OR}_{p\text{-}CO_2H}/k^{OMe}_{p\text{-}CO_2H}$.

Mol. proptn., ether : Cl_2.	R = Me.	Et.	Pr^{α}.	Pr^{β}.	Bu.	CH_2Ph.
1 : 1	100	197	—	444	224	70
3 : 1	100	198	215	445	217	71
10 : 1	100	199	—	—	—	68

EXPERIMENTAL.

Reference to the earlier paper of Orton and Bradfield (*loc. cit.*) may be made for all details of the velocity measurements not now specifically mentioned. The ethers were prepared by standard methods from the corresponding hydroxy-compounds and the alkyl iodide or benzyl chloride. Small amounts of impurities (1% or less) which react slowly or not at all with chlorine do not seriously vitiate the velocity determinations, but even traces of impurities which are reactive towards chlorine exert a marked effect when the proportion of the ether to chlorine is 3 : 1 or 10 : 1. The materials were therefore repeatedly recrystallised, if solid, or, if liquid, submitted to slow fractional distillation under a pressure of 1—2 mm., until the velocity coefficient for the substance was unchanged by further purification. This was taken as our standard of purity, and was not always readily attained. Particular difficulty was met with in the case of the *p*-chloro-ethers, until a specially purified *p*-chlorophenol, supplied by Messrs. The British Drug Houses, Ltd., was used as a starting material.

The authors wish to express their gratitude to Prof. K. J. P. Orton, F.R.S., for suggesting the subject, and for helpful advice and constructive criticism throughout the research.

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BANGOR. [*Received, March 1st*, 1928.]

CXXXIV.—*Synthesis of Cyclic Compounds. Part II. Ethyl* r- *and* meso-*βγ-Diphenylbutane-ααδδ-tetracarboxylates. Synthesis of a Truxinic Acid.*

By ISRAEL VOGEL.

IN Part I (J., 1927, 1986) the synthesis of ethyl βγ-dimethylbutane-ααδδ-tetracarboxylate, a substance which should theoretically exist in a *meso*- (I) and a racemic form (II), was described. The separation

	$CH(CO_2Et)_2$	$CH(CO_2Et)_2$	
(I.) R = Me	RCH	RCH	(II.) R = Me
(III.) R = Ph	RCH	HCR	(IV.) R = Ph
	$CH(CO_2Et)_2$	$CH(CO_2Et)_2$	

of the two esters (I) and (II) could not be effected owing to the proximity of their boiling points; hydrolysis by alcoholic potash, however, yielded a mixture of the two corresponding stereoisomeric tetracarboxylic acids which was separated into two forms, m. p. 152—154° (decomp.) and 185—185·5° (decomp.), respectively. The *dl*-configuration then provisionally assigned to the less fusible form has now been confirmed by the resolution of the acid into optically active components *via* the strychnine salts, full details of which will be given in a later communication.

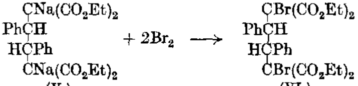
Treatment of the mixture of esters (I) and (II) with sodium methoxide and bromine gave an almost quantitative yield of the corresponding *cyclo*butane compound (compare Perkin, J., 1887, **51**, 1; 1894, **65**, 572), in agreement with the requirements of the Thorpe–Ingold modified strain theory.

The investigation of the analogous βγ-diphenyl compounds was obviously desirable, since it would not only provide a means of studying the effect of two adjacent $\frac{Ph}{H}{>}C{<}^{\theta}$ groups on this method of *cyclo*butane ring formation, but would also lead to a rational synthesis of the truxinic acids. Unfortunately, no calculations of the value of the angle θ are at present available, so that no predictions of the ease of ring formation can be made on purely spatial grounds. It would appear, however, that in addition to the " volume " factor, there is a " polar " factor associated with the phenyl group which must be taken into account.

Henle (*Annalen*, 1906, **348**, 16), on reducing ethyl benzylidenemalonate with aluminium amalgam, was able to isolate only ethyl benzylmalonate. Reduction under the conditions previously described (Vogel, J., 1927, 594) gave, however, in addition to 50—55% of ethyl benzylmalonate, 35—40% of a mixture of two *ethyl*

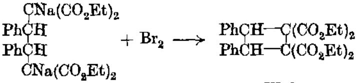
βγ-diphenylbutane-ααδδ-tetracarboxylates. This mixture was quantitatively separated by means of absolute alcohol (see p. 1020) and shown to consist of about 40% of a solid form, m. p. 88°, to which the racemic configuration (IV) is assigned, and about 60% of a liquid *meso*-form (III). Hydrolysis with alcoholic potash gave the two corresponding tetracarboxylic acids, m. p. 219—220° (decomp.) and 182—183° (decomp.), respectively.

Both esters form disodium compounds, the liquid more readily than the solid form, on treatment with a suspension of sodium methoxide in dry ether. Attempts to produce ring closure by means of bromine led to widely different results in the two cases. The *disodium* compound (V) from the solid modification reacted with twice the calculated quantity of bromine required for *cyclo*butane ring formation and gave a nearly quantitative yield of *ethyl* r-*αδ-dibromo-βγ-diphenylbutane-ααδδ-tetracarboxylate* (VI), a crystalline solid, m. p. 180°, the reaction evidently proceeding according to scheme (A). This reaction together with the fact that the solid yields the higher-melting tetracarboxylic acid may be taken as establishing the *dl*-configuration of the ester, m. p. 88°.



(V.) (VI.) (A)

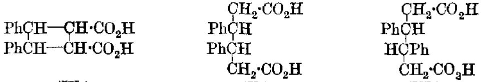
The *disodium* compound (VII) derived from the liquid form, on the other hand, reacted with the calculated quantity of bromine required for *cyclo*butane ring formation (B), presumably with the formation



(VII.) (VIII.) (B)

of the ester (VIII). Hydrolysis of the product with alcoholic potash, which was accompanied by considerable carbonisation and the formation of resinous matter, and subsequent heating at 280° until effervescence ceased gave an extremely poor yield (less than 1%) of an acid, m. p. 239°, which was analysed in the form of its dimethyl ester, m. p. 117°. There is no doubt that this is the *cyclo*butane acid (IX), since the two βγ-diphenyladipic acids, which should theoretically possess the configurations (X) and (XI), melt respectively at 169—170° and 270°, the dimethyl esters melting at 73° and 175° (Henle, *loc. cit.*). These results were confirmed by

treating the mixed disodio-compounds derived from the mixture of esters (III) and (IV) with bromine: the quantity of bromine



(IX.) (X.) (XI.)

required was equal to that calculated on the assumption that 45% of the disodio-compound had reacted according to scheme (A) and the remainder according to (B). The dibromo-ester (VI), which is only slightly soluble in both ether and water, was precipitated on the addition of water, the product of reaction (A), which was identical with that obtained from the *meso*-form, remaining in the ethereal solution.

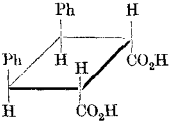
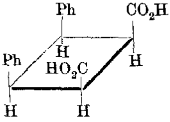
The greater rigidity of structure associated with a molecule containing a phenyl group is clearly shown by these experiments, since the mixture of ethyl *r*- and *meso*-dimethylbutanetetracarboxylates gives an excellent yield of the *cyclo*butane compound, thus showing that inversion must have occurred during ring formation. This rotation is apparently inhibited for the diphenyl compounds and the *r*-dibromo-ester (VI) is produced.

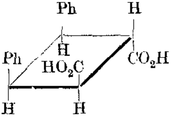
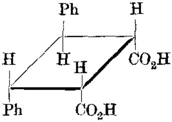
There are six possible configurations for the 2 : 3-*diphenylcyclobutane*-1 : 4-*dicarboxylic acid* (IX), or truxinic acid if the nomenclature of Stoermer (*Ber.*, 1922, **55**, 1868) be adopted. Of these, only four, the β-, δ-, ζ-, and *neo*-acids, have so far been isolated from cinnamic acid by additive ring formation (compare *Ann. Rep.*, 1924, **21**, 96). The melting points of these acids and their dimethyl esters are respectively 209° (decomp.) and 76°, 175° and 77°, 239° and 116°, 209° and 127° (Stoermer and Bachér, *Ber.*, 1922, **55**, 1865). The properties of the synthetical acid and its dimethyl ester are in complete agreement with those which have been described for ζ-truxinic acid and it would appear that they are identical; a direct comparison, however, has not yet been possible.

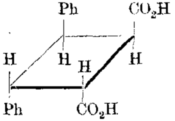
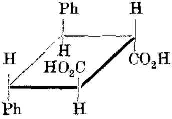
The ζ- and δ- and also the β- and *neo*-acids are related as *cis*- and *trans*-acids.

These two pairs of acids are closely allied to the *cis*- and *trans*-2 : 3-dimethyl*cyclo*butane-1 : 4-dicarboxylic acids described in Part I and it appears reasonable to assign, at least provisionally, configurations to the synthetical acids similar to those deduced for the truxinic acids from the work of Stobbe, Stoermer, de Jong, and their co-workers. The configuration (XV) is assigned to the author's synthetical diphenyl acid and it appears very probable that *cis*- and *trans*-2 : 3-dimethyl*cyclo*butanedicarboxylic acids have configurations

similar to (XV) and (XVII). The constitution, analogous to (XIII), *originally assigned to the cis-acid is now considered less* likely than (XV).

(XII.)


(XIII.)

(XIV.)


(XV.)

(XVI.)


(XVII.)

The very small yield of *cyclo*butane compounds obtained from the ethyl βγ-diphenyl- in contrast with the excellent yields obtained from the unsubstituted (Perkin, *loc. cit.*) and βγ-dimethyl-butanetetracarboxylates (J., 1927, 1985) illustrates the complexity of the problem of explaining the effect of substituents on the *ease of ring formation*. Although this is doubtless due to stereochemical influences such as are postulated by the modified strain theory, the possibility that a polarity factor may play some part must not be overlooked. No experiments have yet been completed on the effect of substituent groups on the *stability* of *cyclo*butane rings, but the results already recorded in the literature are in complete accord with the Thorpe–Ingold theory; for example, Perkin and Simonsen (J., 1909, **95**, 1164) found that whereas fission of the *cyclo*butane ring

$$CO_2H\cdot CH<\begin{matrix}CH_2\\CH_2\end{matrix}>CH\cdot CO_2H \quad \text{(XVIII.)}$$

$$CO_2H\cdot CH<\begin{matrix}CMe_2\\CH_2\end{matrix}>CH\cdot CO_2H \quad \text{(XIX.)}$$

$$\text{(XX.)}\quad \begin{matrix}CH_2-CH\cdot CO_2H\\ | \quad\quad | \\ CH_2-CH\cdot CO_2H\end{matrix}$$

$$\begin{matrix}CHMe\cdot CH\cdot CO_2H\\ | \quad\quad | \\ CHMe\cdot CH\cdot CO_2H\end{matrix}\quad \text{(XXI.)}$$

in *cis-cyclo*butane-1 : 3-dicarboxylic acid (XVIII) could readily be effected by heating with fuming hydrobromic acid in a sealed tube

at 100°, *cis*-norpinic acid (XIX) was attacked neither by this reagent at 120° nor by concentrated sulphuric acid at 100°. It should, however, be mentioned that the stability of the ring is affected by the *relative* positions of the substituent groups round the ring, since it has been shown (Perkin and Simonsen, *loc. cit.*) that the isomeric unsubstituted 1 : 4-dicarboxylic acid is unaffected by heating with fuming hydrobromic acid at 100°. However, in their stability towards different reagents, Perkin's unsubstituted 1 : 4-dicarboxylic acids (XX) may be compared with the author's dimethyl homologues (XXI), and it may be expected on the basis of the modified strain theory that the difference in stability will not be very great but that on the whole (XXI) will be slightly more stable than (XX). It is hoped to test this point in the near future.

The substances being investigated in this series of researches are all conjugated compounds of the general formula $CR_1R_2{:}CR_3R_4$, where R_1,R_2 are groups or ring systems of very varied type and R_3,R_4 are H, CN, CO_2Et, COMe, etc. On reduction with moist aluminium amalgam in ether, two simultaneous and also possibly consecutive reactions take place, *viz.*, (*a*) the addition of hydrogen to the double bond with the production of compounds (XXII), and (*b*) the formation of bimolecular compounds (XXIII). Most of the

(XXII.) $CHR_1R_2{\cdot}CHR_3R_4$

$$\begin{array}{l} CR_1R_2{\cdot}CHR_3R_4 \\ | \\ CR_1R_2{\cdot}CHR_3R_4 \end{array}$$ (XXIII.)

recorded cases (compare ethyl ethylidenemalonate, Higginbotham and Lapworth, J., 1923, **123**, 1618; Vogel, J., 1927, 1985: mesityl oxide, Vogel, J., 1927, 594) have shown that the reaction proceeds almost exclusively in the direction (*b*). The example now described, *i.e.*, the reduction of ethyl benzylidenemalonate, shows clearly that in this instance reactions (*a*) and (*b*) both take place, 50 to 55% of (XXII) and 35—40% of (XXIII) being formed. The extent to which each of these reactions takes place is controlled mainly by the groups R_1, R_2; and it appears that the volume of these groups plays an important part, provided of course that R_3 and R_4 are suitable "activating" groups to enable the reduction to take place at all. It seems that the larger the volume of R_1,R_2 the more reaction (*a*) takes place in preference to (*b*). This view receives support from the fact that ethyl α-cyano*cyclo*hexylideneacetate gives about 80% of ethyl *cyclo*hexylcyanoacetate and 5—10% of a solid which is probably of type (XXIII). Full details of this and analogous cases will be given in a subsequent communication.

The mechanism of the reduction of unsaturated compounds in ethereal solution by moist aluminium amalgam adopted by the author is based on that originally suggested by Higginbotham and

Lapworth (*J.*, 1923, **123**, 1618). The unsaturated compound is first adsorbed on the surface of the metal and reaction takes place at the surface, where chemical forces are known to be very powerful. Two modes of reaction corresponding to (*a*) and (*b*) are possible and may be represented as follows:

$$(a)\quad \mathrm{M} + CR_1R_2{:}CR_3R_4 \longrightarrow \mathrm{M}\,CR_1R_2{:}CR_3R_4 \xrightarrow{2H_2O} \mathrm{M}^{++} + CHR_1R_2{\cdot}CHR_3R_4 + 2OH^-$$

$$(b)\quad \left.\begin{array}{l} \mathrm{M}\,CR_1R_2{:}CR_3R_4 + CR_1R_2{:}CR_3R_4 \\ \text{and/or}\quad \mathrm{M} + 2CR_1R_2{:}CR_3R_4 \end{array}\right\rangle \longrightarrow \mathrm{M}\begin{array}{l} CR_1R_2{:}CR_3R_4 \\ CR_1R_2{:}CR_3R_4 \end{array} \xrightarrow{2H_2O} \mathrm{M}^{++} + \begin{array}{l} CR_1R_2{\cdot}CHR_3R_4 \\ | \\ CR_1R_2{\cdot}CHR_3R_4 \end{array} + 2OH^-$$

This "adsorption" theory receives support from the fact that the yields of reduction product under otherwise comparable conditions are controlled by the thickness, and therefore the surface, of the aluminium foil employed in the preparation of the amalgam. Further, there is always an initial period of induction and this is doubtless associated with the adsorption of the unsaturated compound. The mechanism suggested by Cohen (*Rec. trav. chim.*, 1919, **38**, 113) involving the initial addition of a hydrogen atom to the carbonyl oxygen with the formation of a tervalent carbon derivative which subsequently polymerises with the formation of a bimolecular compound, and also his explanation of the production of the unimolecular reduction product by fission of the bimolecular compound, are considered improbable. This mechanism has been adopted by Steinkopf and Wolfram (*Annalen*, 1923, **430**, 128) as a general explanation of the reduction of unsaturated compounds, although these authors assume that the unimolecular compound is produced by the reduction of the free radical. The present author's view is that the mechanism of the reduction depends on the nature of the reducing agent and that while the "free radical" theory may or may not hold for other types of reduction (compare Conant and Cutter, *J. Amer. Chem. Soc.*, 1926, **48**, 1026, who found that mesityl oxide is not reduced by vanadous or chromous chloride, the operation of another mechanism thus being indicated), all the results of experiments on reduction with aluminium amalgam in ethereal solution are in complete agreement with the "adsorption" theory outlined above.

EXPERIMENTAL.

Ethyl benzylidenemalonate was prepared by condensing freshly distilled benzaldehyde with ethyl malonate in the presence of

piperidine (Knoevenagel, *Ber.*, 1898, **31**, 2585). The pure substance boiled at 180°/14 mm. and had $d_{4^\circ}^{18\cdot4^\circ}$ 1·1048 and $n_{D}^{18\cdot4^\circ}$ 1·53795 (supercooled liquid).

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl meso- *and* r-*βγ-Diphenylbutane-ααδδ-tetracarboxylates* (III and IV).—Ethyl benzylidenemalonate (150 g.) was reduced by moist aluminium amalgam (200 g.) (Vogel, J., 1927, 594). The product, after being worked up in the usual manner, was fractionated under diminished pressure (water-pump); 75—80 g. were collected up to 205°/20 mm. (mainly at 174—178°/17 mm.) and the pressure then began to fall. The residue (60—65 g.), a dark red, extremely viscid mixture of the *meso*- and *r*-esters (III) and (IV) which partly crystallised on standing, was distilled (oil-pump) as rapidly as possible, in order to reduce carbonisation to a minimum. A very small quantity distilled at 245—255°/3 mm. The main fraction, b. p. 255—270°/3 mm., an almost colourless, viscid liquid which darkened on exposure to the atmosphere, partly crystallised when left over caustic potash in a vacuum desiccator for 24 hours. After the adhering oil had been removed by draining on tile and trituration with absolute alcohol, *ethyl* r-*βγ-diphenylbutane-ααδδ-tetracarboxylate* was obtained in beautiful crystals, m. p. 88° (Found: C, 67·3; H, 6·8. $C_{28}H_{34}O_8$ requires C, 67·5; H, 6·9%).

The *meso*-ester was isolated as a viscid red oil by extracting the porous tiles with ether and was analysed in the form of the corresponding tetracarboxylic acid (*vide infra*).

The fraction of low b. p. obtained from the reduction product, on redistillation, gave ethyl benzylmalonate, b. p. 163°/14 mm., $d_{4^\circ}^{20\cdot0^\circ}$ 1·0750, $n_{D}^{20\cdot0^\circ}$ 1·4872 (Found: C, 67·3; H, 7·2. Calc.: C, 67·2; H, 7·2%), which was hydrolysed by alcoholic potash to benzylmalonic acid; this, after crystallising from benzene, melted, alone or mixed with an authentic specimen prepared from benzyl chloride and ethyl sodiomalonate, at 120° (decomp.). Henle (*loc. cit.*) gives m. p. 114—115°.

Hydrolysis of the r-*Ester* (IV).—A mixture of 5 g. of the solid ester, 10 g. of absolute alcohol, and 4 g. of caustic potash in 8 g. of water was refluxed for 5 hours and then evaporated to dryness. A solution of the residue in a little water was extracted with ether to remove unchanged ester, if present, and acidified with dilute sulphuric acid, and the precipitated r-*acid* was washed with water and freed from potassium sulphate by dissolution in warm acetone and from a small quantity of the *meso*-acid by washing with dry ether; it then melted at 219—220° (decomp.) (Found: C, 62·5; H, 4·9; equiv. by titration, 98. $C_{20}H_{18}O_8$ requires C, 62·2; H, 4·7%; equiv., 96·5).

Preparation of the meso-*Acid.*—The thick oil obtained by ether extraction of the porous tiles in the separation of the *r*-ester was hydrolysed exactly as described for the *r*-ester. The *meso-acid* had m. p. 182—183° (slight softening at 172°) (Found: C, 62·2; H, 4·8%; equiv. by titration, 97).

Quantitative Separation of the meso- *and* r-*Esters* (III and IV).—The redistilled ethyl diphenylbutanetetracarboxylate mixture (32 g.) was agitated with about an equal weight of absolute alcohol. The *r*-ester, which rapidly crystallised after several hours, was collected and washed with absolute alcohol; further crops were obtained by concentrating the filtrate at room temperature under reduced pressure until no more crystals would separate. The final liquor consisted of practically pure *meso*-ester. In this way 13 g. of the *r*-ester and 19 g. of the *meso*-ester (a red viscid oil, weighed after being kept in a vacuum over concentrated sulphuric acid for a week) were obtained.

Reaction of the Disodio-compound (V) *of Ethyl* r-*βγ-Diphenylbutane-ααδδ-tetracarboxylate with Bromine. Formation of Ethyl* r-*αδ-Dibromo-βγ-diphenylbutane-ααδδ-tetracarboxylate* (VI).—To 0·80 g. of "molecular" sodium under 100 c.c. of dry ether, 1·45 c.c. of dry methyl alcohol were added. When all the sodium had reacted (gentle warming was necessary), a solution of the *r*-ester (IV) (8·3 g.) in dry ether (175 c.c.) was added. The *disodio*-compound (V) gradually separated and after 12 hours it was filtered off, washed rapidly with absolute ether containing a little absolute alcohol, and dried over concentrated sulphuric acid in a vacuum (Found: Na, 8·7. $C_{28}H_{32}O_8Na_2$ requires Na, 8·5%).

In another experiment in which the same quantities were employed, the suspension of the disodio-compound in ether was stirred mechanically, and dry bromine (2·0 c.c.) slowly added; a yellow colour indicative of the presence of excess of bromine, which could also be identified by its odour, became apparent after 1·90 c.c. had been added (calc. according to reaction A, p. 1014, 1·88 c.c.). The stirring was continued for 3 hours, water was then added, the resultant solution filtered, and the residue (4·0 g., m. p. 174°) washed with water and with ether; it then crystallised from ethyl acetate in colourless, glistening plates, m. p. 180° (Found: C, 51·0; H, 4·9; Br, 24·7. $C_{28}H_{32}O_8Br_2$ requires C, 51·2; H, 4·9; Br, 24·4%). The ethereal solution was washed with dilute sodium carbonate solution and with water, dried with anhydrous sodium sulphate, and evaporated. The pale red, viscid residue (7 g.) crystallised almost completely when left in contact with absolute alcohol over caustic potash in a vacuum desiccator; after being washed with alcohol and recrystallised from ethyl acetate, it melted at 180° and was

identical with the precipitated solid. No other reaction product could be isolated.

Reaction of the Disodio-compound (VII) *of Ethyl* meso-$\beta\gamma$-*Diphenylbutane*-$\alpha\alpha\delta\delta$-*tetracarboxylate with Bromine. Synthesis of a* 2 : 3-*Diphenyl*cyclo*butane*-1 : 4-*dicarboxylic Acid* (*Truxinic Acid*) (IX).—The *disodio*-compound (VII) was prepared, exactly as described for the *r*-compound, as a pale yellow solid (Found: Na, 8·6%). The quantities employed in a particular experiment were 1·25 g. of "molecular" sodium, 2·25 c.c. of dry methyl alcohol, and 12·7 g. of ester in 100 c.c. of absolute ether. The suspension of the disodio-compound in dry ether was mechanically stirred and slowly treated with dry bromine: excess of bromine was apparent when 1·40 c.c. had been added (calc. for *cyclo*butane ring formation according to reaction B, p. 1014, 1·39 c.c.). Water was added after 3 hours' stirring, and no solid remained undissolved (compare *r*-compound). After the product had been worked up in the usual manner, 12 g. of a viscid, dark red oil remained. This was hydrolysed by heating on the steam-bath for 18 hours with twice the calculated quantity of ethyl-alcoholic potash, and the solution evaporated to dryness. A solution of the residue in water was filtered to remove carbonaceous matter and then cautiously acidified with ice-cold dilute sulphuric acid. The precipitated resinous matter was removed by filtration and the filtrate was saturated with ammonium sulphate and extracted seven times with ether. The ethereal solution, dried with anhydrous sodium sulphate and evaporated, yielded a pale yellow, oily solid which crystallised almost completely when left in contact with light petroleum (b. p. 40—60°). The slightly gummy, hygroscopic solid was heated at 280° until effervescence ceased, and the residue was fractionally crystallised from acetone; it was thus possible to isolate a solid, which melted at 239°. It was found best, however, to esterify the product with methyl alcohol and sulphuric acid and treat the brown gummy esterification product with large quantities of light petroleum (b. p. 40—60°); on allowing the latter to evaporate, a somewhat oily crystalline solid was obtained. This was drained on tile and recrystallised from dilute methyl alcohol; it then melted at 117°. By repeating this process with the resinous matter, which gradually solidified, obtained on acidifying the alkaline solution, further small quantities of the ester, m. p. 117°, could be obtained. The total yield of pure ester in one experiment rarely exceeded a few mg. (Found: C, 74·0; H, 6·2. $C_{20}H_{20}O_4$ requires C, 74·1; H, 6·2%).

Reaction of Bromine with the Disodio-compounds of the Mixture of Ethyl meso- *and* r-$\beta\gamma$-*Diphenylbutane*-$\alpha\alpha\delta\delta$-*tetracarboxylates*.—The mixture of the esters was converted into the disodio-compounds

(2·25 g. of "molecular" sodium, 100 c.c. of ether, 4·00 c.c. of methyl alcohol, 22 g. of mixed esters, b. p. 240—265°/3 mm., in 100 c.c. of ether). On treatment with bromine excess was just apparent when 3·65 c.c. had been added [Calc. for reaction (A), 5·00 c.c.; for reaction (B), 2·50 c.c.; for 45% of (A) and 55% of (B), 3·63 c.c.]. On the addition of water the dibromo-compound (VI) was precipitated, and from the filtrate, which behaved exactly as described for the *meso*-form, a few mg. of the dimethyl ester, m. p. 117°, were isolated.

In conclusion, my thanks are tendered to Professor J. F. Thorpe, F.R.S., for his kind encouragement, to the Trustees of the Beit Scientific Research Fellowships for a Fellowship, and to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of the research.

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CXXXV.—*The Constitution of Irigenin and Iridin. Part I.*

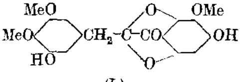
By WILSON BAKER.

THE glucoside iridin * contained in the dried rhizomes of the *Iris florentina* has been carefully examined by de Laire and Tiemann (*Ber.*, 1893, **26**, 2010), who found that on hydrolysis with dilute acid it gave one molecule of glucose and one molecule of irigenin, a phenolic substance of empirical formula $C_{18}H_{16}O_8$. This compound gave an impure dibenzoyl derivative by the Schotten–Baumann reaction and a so-called diacetyl derivative which readily underwent partial hydrolysis with production of a "monoacetylirigenin." Decomposition with aqueous potassium hydroxide in an atmosphere of hydrogen gave one molecule of iridic acid (3-hydroxy-4 : 5-dimethoxyphenylacetic acid), one molecule of iretol (methoxyphloroglucinol), and one molecule of formic acid. These authors assigned to it the formula (I).

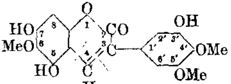
The formulation of irigenin by (I) is, however, not justified by the experimental evidence, no satisfactory proof being offered that

* This compound must not be confused with the "iridin" of the Pharmacopœia ("The Extra Pharmacopœia," Martindale and Westcott, 17th ed., 1920, p. 802), which is a dark brown, powdered resin, obtained by extraction of the root of the North American "blue flag" (*Iris versicolor*) with 60% alcohol. An examination of its constituents by Power and Salway (*Amer. J. Pharm.*, 1911, **83**, 1) showed that it was entirely lacking in the glucoside iridin.

the two aromatic nuclei are united through a straight chain of three carbon atoms. The essential correctness of the work has been borne out by the syntheses of iridic acid by Mauthner (*Annalen*, 1926, **449**, 102) and of iretol by Kohner (*Monatsh.*, 1899, **20**, 928).



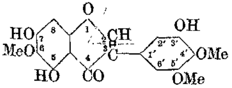
(I.)



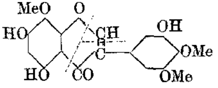
(II.)

Bargellini has recently expressed the view (*Gazzetta*, 1925, **55**, 945) that irigenin should be regarded as a coumarin derivative (II). Although such a structure would account for most of its properties, including its decomposition by alkali (see Bargellini, *loc. cit.*; Baker, J., 1925, **127**, 2351), yet the production of de Laire and Tiemann's dibenzoyl derivative cannot readily be interpreted by this formula (de Laire and Tiemann's diacetyl- and monoacetyl-irigenin are referred to later); for (II) should give a tribenzoyl derivative, since the hydroxyl group occupying position 5 in coumarins of this type (unlike chromones, see below) possesses normal phenolic properties (see 5 : 7 : 4′-trihydroxy-4-phenylcoumarin, Bargellini, *Atti R. Accad. Lincei*, 1925, **2**, 32; 5 : 7-dihydroxy-3-phenylcoumarin, Bargellini, *Gazzetta*, 1927, **57**, 461; 5 : 7 : 4′-trihydroxy-3-phenylcoumarin, Bargellini and Monti, *ibid.*, p. 464).

It seemed much more probable that irigenin should be represented by one of the formulæ (III) and (IV) as belonging to the *iso*flavone



(III.)



(IV.)

(3-phenylchromone) group, two members of which, genistein and prunetin, are now known to occur in nature (Baker and Robinson, J., 1925, **127**, 1981; 1926, 2713). These formulæ represent irigenin as possessing *three* phenolic hydroxyl groups, one of which, occupying position 5 ortho to the carbonyl group, would have very weak phenolic properties, not forming an alkali salt in aqueous solution and being difficult to methylate with methyl iodide, but which would yet give a positive ferric chloride reaction and an easily hydrolysable acetyl derivative. Thus the formation of the dibenzoyl derivative is satisfactorily accounted for owing to the weakly phenolic nature of the hydroxyl group in the 5-position.

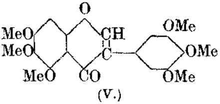
The starting material used in the present investigation was the

"Florentine Orris Root" of commerce, a supply of the finely powdered rhizomes being obtained through Messrs. James Woolley, Sons and Co., Ltd., Manchester. According to Parry ("The Chemistry of Essential Oils and Artificial Perfumes," 3rd ed., Vol. I, p. 92) and other authorities, commercial florentine orris root is a mixture of the rhizomes of three species of iris, *Iris germanica, Iris pallida,* and to a lesser extent *Iris florentina.* It seems doubtful whether de Laire and Tiemann's material consisted solely of the rhizomes of the last species, as the florentine orris root has often been erroneously assumed to be synonymous with the *Iris florentina*.

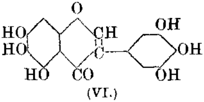
de Laire and Tiemann give very scanty details for the isolation of the glucoside iridin, and the yield is not stated, but it was probably poor, as it was necessary to have the preliminary operations carried out on the works scale. Attempts to follow their method gave only hopelessly bad results, so the problem had to be reinvestigated. A satisfactory process for the extraction of iridin has now been worked out, and in a large number of consecutive experiments the yields averaged just over 0·9% on the weight of the root. It is safe to say that iridin *occurs* to the extent of 1% in florentine orris root. Irigenin is easily prepared by hydrolysis of iridin with dilute sulphuric acid, and is now shown to be dimorphous. The formula $C_{15}H_7O_5(OMe)_3$ was confirmed, and the experiments now described prove conclusively that irigenin possesses the structure (III).

Irigenin very closely resembles the known naturally occurring and synthetical members of the *iso*flavone group. This is evident from its reactions with ferric chloride, dilute alkalis and sulphuric acid (experimental section), and from its dyeing properties (below). The dibenzoyl derivative possesses the properties previously described, except that it melts at 155—160° (de Laire and Tiemann give m. p. 123—126°, probably an error for 153—156°). The substance is impure, but undoubtedly consists essentially of dibenzoylirigenin, since it is insoluble in alkali and gives a positive ferric chloride reaction. The "diacetylirigenin" prepared as described by heating with acetic anhydride and sodium acetate in a sealed tube, or more readily by boiling with acetic anhydride under reflux, melts, when pure, at 127—128° (recorded m. p. 122°). It gives no colour reaction with ferric chloride, and an acetyl determination showed it to be *triacetylirigenin* (disproof of formula I), with which the previous carbon and hydrogen determinations agree. The "monoacetylirigenin" of m. p. 169° is hence *diacetylirigenin,* with which their analysis agrees, its formation being obviously due to the known ready hydrolysis of the 5-acetoxy-group in chromones (see 5 : 7 : 4′-triacetoxy-2-methyl*iso*flavone, Baker and Robinson, *J.*, 1926, 2716), and it is therefore 7 : 3′-*diacetylirigenin*.

Vigorous methylation of irigenin with methyl sulphate readily gives a characteristic *irigenin trimethyl ether* (V) (disproof of formula I). The position of the methoxy-groups in the tetrahydroxybenzene nucleus is proved by decomposition of the ether with alkali, whereby 3 : 4 : 5-trimethoxyphenylacetic acid and antiarol (3 : 4 : 5-trimethoxyphenol) are formed.



(V.)

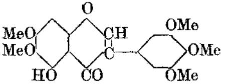


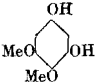
(VI.)

Demethylation of irigenin produces the hexahydric phenol (VI), which may be termed *irigenol*. This substance is oxidised with extreme readiness in alkaline solution, gives a *hexa-acetyl* derivative, a *hexamethyl ether* identical with (V), and a crystalline, orange *oxonium sulphate*, $C_{15}H_{10}O_8,H_2SO_4$. The formation of the last compound proves that irigenin cannot be represented as a coumarin (II).

Methylation of irigenin with three molecules of methyl iodide and alkali in a sealed tube gives *irigenin* 7 : 3′-*dimethyl ether* (VII), though with an excess of the reagents the product is a mixture of (VII) and the trimethyl ether (V), and under certain conditions a third compound, m. p. 154·5°, is produced. This dimethyl ether

(VII.)



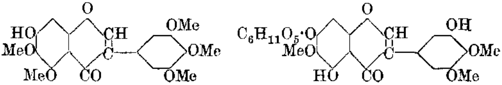


(VIII.)

has very weak phenolic properties, being insoluble in sodium hydroxide solution even on warming, a behaviour which is inexplicable on the basis of formula (II), and establishes the position of the free hydroxyl group. It gives a positive reaction with ferric chloride, an *acetyl* derivative, and by methylation with methyl sulphate in methyl-alcoholic solution, irigenin trimethyl ether (V). Decomposition with aqueous alkali at 100° in hydrogen gives 3 : 4 : 5-trimethoxyphenylacetic acid and 4 : 5-dimethoxyresorcinol (VIII). These results prove that irigenin possesses the formula (III), and is consequently 5 : 7 : 3′-*trihydroxy*-6 : 4′ : 5′-*trimethoxy*iso*flavone*.

The position of the glucose nucleus in iridin was established in the following way. Methylation of iridin in methyl alcohol with an excess of diazomethane gave a resinous, methylated glucoside; this on hydrolysis yielded an irigenin dimethyl ether, possessing normal phenolic properties, which reacted readily with methyl sulphate

to give irigenin trimethyl ether (V). Decomposition with alkali gave the same products as were given by its isomeride (VII), namely, 3 : 4 : 5-trimethoxyphenylacetic acid and 4 : 5-dimethoxyresorcinol (VIII). This *substance must therefore be irigenin 5 : 3′-dimethyl ether* (IX), and the glucoside iridin hence has the constitution (X) with the glucose nucleus in the 7-position.



(IX.) (X.)

The 5 : 6 : 7-structure of the tetrahydroxybenzene nucleus in irigenin is similar to that occurring in a few other natural products, the flavones scutellarein (see Bargellini, *Gazzetta*, 1919, **49**, ii, 47) and baicalein (Shibata, Iwata, and Nakamura, *Acta Phytochim.*, 1923, **1**, 105), the salts of the anhydrobenzopyranol base carajuretin, and probably the flavonol quercetagetin (Chapman, Perkin, and Robinson, J., 1927, 3015). The position of the glucose nucleus in iridin is the same as is probably occupied by the sugar nucleus in the flavone glucosides (Tasaki, *Acta Phytochim.*, 1925, **2**, 129), and lends support to the view, first suggested to the author by Professor R. Robinson some years ago, that in the *iso*flavone prunetin the methoxy-group occupies position 4′, and not position 7 as originally proposed by Finnemore (*Pharm. J.*, 1910, **31**, 604).

The dyeing properties of irigenin are very similar to those of the naturally occurring flavones, and of the *iso*flavone genistein (prunetol) in particular. Irigenin gives on woollen cloth mordanted with aluminium, tin, chromium, and iron, very pale yellow, exceedingly pale yellow, light yellowish-olive, and chocolate-brown colours, respectively. Iridin, with aluminium and tin mordants, gives almost the same colours as irigenin, but iron-mordanted wool is dyed a much paler brown, and with chromium mordant a paler, greyish-olive is produced. Addition of powdered chalk to the dye-bath gives brighter shades. Irigenol is a much more powerful dye than either iridin or irigenin, as might be expected from the fact that it contains two pyrogallol groupings. With the above-mentioned mordants it gives light yellow, bright yellow, yellow-brown, and olive-black colours, respectively.

Synthetical experiments in connexion with irigenin are in progress.

EXPERIMENTAL.

Iridin (X).—Powdered orris root (1 kg.) is boiled under reflux for ½ hour with alcohol (2 l.), and the extract filtered while hot

from the residue of starch, which is well pressed down and drained. The pale brown extracts from two experiments are distilled until the residue boils frothily (volume about 300 c.c.); it is then poured into a stirring jar. On standing, or preferably on seeding and stirring from time to time, the glucoside slowly separates, giving a thick, crystalline paste. After at least 48 hours alcohol (200 c.c.) is added and the mixture stirred for about 10 minutes; then, after standing, the glucoside settles to the bottom of the vessel and the dark brown, supernatant, alcoholic solution is poured off. The glucoside is again stirred with alcohol (200 c.c.) and the process repeated with a further quantity of alcohol (100 c.c.), and then with ether (100 c.c.). The mixture consisting of iridin and a large amount of glucose usually clots together after the first washing with alcohol and the mass may then have to be worked by hand. The very thick, pale yellowish, viscous material is stirred with water (250 c.c.) until the glucose dissolves, leaving a milky white suspension of the iridin, which is filtered, washed thoroughly with cold water, and dried on the steam-bath, whereby it acquires a very slight yellow colour. The yield of this almost pure glucoside from 2 kg. of the powdered rhizomes is about 18 g. The iridin may be recrystallised from a large volume of alcohol, or, better, from 50% methyl alcohol.

An alcoholic solution of iridin develops with a trace of ferric chloride a somewhat intense, dull reddish-violet colour, changing to dull olive-green with excess. It dissolves in concentrated sulphuric acid to a yellow solution which, on heating to 100°, rapidly darkens and chars, and iridin is thus easily distinguished from irigenin, whose pale yellow solution is unaltered under these conditions.

Irigenin (III).—Iridin (30 g., not recrystallised), water (35 c.c.), alcohol (45 c.c.), and concentrated sulphuric acid (3 c.c.) are heated in a pressure flask at 100° for 5 hours with occasional shaking. The product is poured into a mixture of alcohol (200 c.c.) and water (100 c.c.), boiled with charcoal, filtered, and treated again with charcoal after addition of water (100 c.c.) (compare de Laire and Tiemann). The filtrate slowly deposits yellowish crystals (about 17 g.), and a further small quantity separates on dilution of the mother-liquor. By recrystallisation from hot, dilute alcohol irigenin is first deposited in very pale yellow, almost rectangular plates, m. p. 185° (Found*: C, 59·9; H, 4·5. Calc. for $C_{18}H_{16}O_8$: C, 60·0; H, 4·4; 3MeO, 25·8%), and later in tiny bunches of pointed needles having the same melting point (Found*: C, 59·9; H, 4·6; MeO, 24·3%). The plate form crystallises unchanged from alcohol, but gives the needle form on recrystallisation from either dilute alcohol or dilute acetic acid. Irigenin gives a ferric chloride reaction

similar to that of iridin. Its non-fluorescent solutions in dilute aqueous sodium hydroxide and concentrated sulphuric acid are very pale yellow, and on dilution of the latter the colour is discharged and irigenin separates unchanged.

Benzoylation of Irigenin.—An alkaline solution of irigenin was shaken with excess of benzoyl chloride below 15°, and the oily product fractionally precipitated from warm benzene by the addition of ligroin. The first dark portion was rejected and then a colourless oil and a flocculent material separated, which were dissolved in much hot alcohol. On cooling, flocks separated and on the first appearance of crystals the solution was rapidly filtered; it then deposited colourless, compact, stellar bunches of tiny needles. m. p. 155—160° with previous softening [Found : C, 66·0; H, 4·2. Calc. for $C_{18}H_{14}O_8(COPh)_2$: C, 67·6; H, 4·2%]. This product is insoluble in caustic alkalis and gives an olive-green colour with ferric chloride in alcoholic solution, and is doubtless a mixture consisting essentially of 7 : 3′-*dibenzoylirigenin*. Attempts to prepare an acetyl derivative gave a white, non-homogeneous, crystalline powder, m. p. 155—165°, which gave no reaction with ferric chloride.

Triacetylirigenin.—Irigenin (5 g.) was boiled under reflux with acetic anhydride (20 c.c.) for 5 hours. The product, isolated after the addition of water and shaking, was recrystallised from dilute acetic acid and obtained in tiny, colourless prisms, m. p. 127—128° [Found (C and H by de Laire and Tiemann) : C, 59·3; H, 4·7; Ac, 26·6. $C_{18}H_{13}O_5(OAc)_3$ requires C, 59·3; H, 4·5; Ac, 26·5%]. The acetyl estimation was carried out by Wenzel's method (*Monatsh.*, 1897, **18**, 659) by decomposition with dilute sulphuric acid and estimation of the acetic acid. de Laire and Tiemann estimated the acetyl groups (Found : Ac, 21·4%) by hydrolysis with dilute alkali, and made an approximate correction for the formic acid produced by decomposition of the irigenin; this correction, however, was certainly too great, as irigenin only slowly decomposes even on treatment with concentrated alkali solution. The double compound with chloroform prepared by precipitating its solution in chloroform with ligroin has an indeterminate composition, since it rapidly loses chloroform (Found in freshly prepared substance : Cl, 7·2. After exposure to the air for 3 days : Cl, 3·5%). It melts at 82° to a frothy, viscous melt with partial loss of chloroform.

The "monoacetylirigenin," m. p. 169°, is really 7 : 3′-*diacetylirigenin* (Found by de Laire and Tiemann : C, 59·8; H, 4·7. Diacetylirigenin, $C_{22}H_{20}O_{10}$, requires C, 59·5; H, 4·5%).

Irigenin Trimethyl Ether (V).—Irigenin (10 g.) was shaken alternately with 10% potassium hydroxide solution (200 c.c.) and methyl sulphate in small portions at about 60°. The solid which finally

separated from the alkaline solution was collected, washed, and crystallised from alcohol (charcoal), in which it was easily soluble when hot, but very sparingly soluble when cold. After a further crystallisation from alcohol, it was obtained in colourless, highly refracting prisms, m. p. 163° (Found* : C, 62·8 ; H, 5·7 ; MeO, 44·6. $C_{21}H_{22}O_8$ requires C, 62·7 ; H, 5·5 ; 6MeO, 46·3%). (The methylated derivatives of irigenin gave variable and low values for carbon by ordinary analytical methods, probably owing to the formation of methane—compare Bradley and Robinson, J., 1926, 2361 ; Oxford and Raper, J., 1927, 421—but good results were obtained by micro-analytical methods—marked*—carried out at especially high temperatures.) As prepared above, and even after many recrystallisations from ethyl or methyl alcohol, this apparently pure irigenin trimethyl ether gives an exceedingly faint ferric chloride reaction. By treating its slightly warm solution in absolute methyl alcohol with diazomethane it is obtained of the same melting point, but now gives no ferric chloride reaction. Thus treated, it shows the curious property of turning very faintly brown on exposure to light.

Decomposition of Irigenin Trimethyl Ether with Alkali.—Irigenin trimethyl ether (6 g.), methyl-alcoholic potash (24 c.c. of 20%), and water (2 c.c.) were heated during 2 hours until the temperature slowly rose to 180° and the methyl alcohol distilled off. The product was dissolved in water (150 c.c.), almost neutralised, saturated with carbon dioxide, and filtered, and the filtrate was repeatedly extracted with ether. The extracts yielded a colourless substance (1·5 g.), which crystallised from a small amount of hot water, containing a little sulphur dioxide, in almost rectangular, irregular plates, m. p. 147° ; these were identified as antiarol (Found : MeO, 47·8. Calc. : MeO, 50·5%). The *O*-acetyl derivative (Chapman, Perkin, and Robinson, *loc. cit.*) crystallised very readily from ligroin in flat, lustrous needles, m. p. 74° (Found : C, 58·4 ; H, 6·2. Calc. : C, 58·4 ; H, 6·2%), and the *O*-benzoyl derivative from alcohol in lustrous, flat needles, m. p. 117° (Kiliani, *Arch. Pharm.*, 1896, **234**, 443). (The remarkable ease of oxidation of antiarol to 2 : 6-dimethoxybenzoquinone does not seem to have been recorded. When a drop of ferric chloride is added to its aqueous solution a transient green colour is produced, which reappears with each drop of the reagent till finally bright yellow needles of the quinone separate, m. p. 256°. This is reduced by sulphur dioxide to 2 : 6-dimethoxyquinol, m. p. 158°.) The liquor remaining after the ether extractions was acidified, and further extractions yielded a carboxylic acid (2·5 g.) which crystallised from hot water in colourless, flat prisms, m. p. 120°, and possessed all the properties of 3 : 4 : 5-trimethoxyphenylacetic acid.

Irigenol (VI).—Irigenin (10 g.) was demethylated with hydriodic acid (100 c.c.; *d* 1·7) at 130° for 1 hour. Crystals separated during the latter part of the reaction and were isolated by the addition of water and filtration. The substance crystallises slowly from 50% acetic acid in pale yellow, microscopic needles, m. p. 331° (decomp.; rapid heating) (Found: C, 53·3; H, 3·9. $C_{15}H_{10}O_8,H_2O$ requires C, 53·6; H, 3·6%). The water of crystallisation is not lost at 140°. *Irigenol* is very sparingly soluble in acetic acid, water, ethyl alcohol, benzene, and ethyl acetate, but dissolves more readily in a mixture of the first two solvents and also in acetone. In the complete absence of air it dissolves in aqueous sodium hydroxide to a yellow, stable solution which deposits unchanged irigenol on acidification, but in the presence of air the solution rapidly assumes an intense crimson colour, and acids now throw down a dark, flocculent precipitate, and the crimson colour only weakly returns when the solution is again made alkaline. Irigenol dissolves in aqueous sodium carbonate to a yellow solution, which slowly turns red in presence of air. Its alcoholic solution develops with a little ferric chloride an intense olive-green colour, changed by excess to a deep reddish-brown, and when treated with a trace of sodium amalgam gives green flocks, a reaction which is shown by scutellarein and baicalein (Bargellini, *Gazzetta*, 1919, **49**, ii, 47). Methylation with methyl sulphate and alkali in an atmosphere of hydrogen readily gave irigenin trimethyl ether (V), m. p. 162°. The *hexa-acetyl* derivative separates after irigenol has been boiled with an excess of acetic anhydride and a few drops of pyridine for 4 hours. Recrystallisation from acetic anhydride gives colourless, microscopic prisms, m. p. 237—238° [Found: C, 57·1; H, 4·1; Ac, 43·9. $C_{15}H_4O_2(OAc)_6$ requires C, 56·8; H, 3·9; Ac, 44·2%].

Irigenol Sulphate.—Irigenol, in common with all irigenin derivatives and other *iso*flavones, dissolves in concentrated sulphuric acid to a yellow solution, which on dilution becomes colourless and deposits the unchanged substance. This general reaction is doubtless due to the formation of coloured oxonium sulphates. Owing to the very sparing solubility of irigenol in acetic acid, the sulphate cannot be prepared by addition of sulphuric acid to this solution. It is best prepared by dissolving irigenol (1 g.) in cold, concentrated sulphuric acid (5 c.c.) and adding glacial acetic acid (20 c.c.); the solution shortly becomes turbid, and after 12 hours is thick with microscopic, orange crystals, which are collected, washed with acetic acid, and dried in a vacuum over soda-lime (Found as hydrate by decomposition with water: $C_{15}H_{10}O_8$, 76·6. $C_{15}H_{10}O_8,H_2SO_4$ requires $C_{15}H_{10}O_8$, 76·4%). *Irigenol sulphate* reacts instantaneously with cold water, the bright orange colour

changing to the yellow of irigenol, and it also decomposes when heated under acetic acid. When dry, it is stable at 135°.

Irigenin 7 : 3'-*Dimethyl Ether* (VII).—Methylation of irigenin by boiling under reflux with an excess of methyl iodide and alkali led to very poor yields of (VII), the product being largely the trimethyl ether (V), though under certain conditions it consisted wholly or chiefly of a third substance, m. p. 154·5° (see below). With three molecules of alkali, the product was almost entirely alkali-soluble, but in a sealed tube satisfactory results were obtained.

Irigenin (5 g.), methyl iodide (3 mols.), and a solution of sodium methoxide (3 mols.) in methyl alcohol (30 c.c.) were heated in a sealed tube at 100° for 16 hours. After cooling, the product was crushed, treated with dilute alkali solution for 24 hours, washed well, and dried. It was then dissolved in hot methyl alcohol (240 c.c.) and the pale yellow needles which separated were filtered off after an hour (yield 1·5 g.). After several recrystallisations from methyl alcohol, it was obtained in tiny, lustrous, pale yellow needles, m. p. 166—167° (Found* : C, 61·7 ; H, 5·4 ; MeO, 38·4. $C_{20}H_{20}O_8$ requires C, 61·8 ; H, 5·2 ; 5MeO, 39·9%).

Irigenin 7 : 3'-*dimethyl ether* in alcoholic solution gives with a trace of ferric chloride an intense violet colour, changing to olive-green with excess. It is insoluble in warm, aqueous sodium hydroxide, but if to its suspension in methyl alcohol a drop of methyl-alcoholic potash is added it at once dissolves with a bright yellow colour, which fades when the solution is diluted with water and at the same time the dimethyl ether separates unchanged. By vigorous treatment with methyl sulphate in methyl-alcoholic potash, it was partly converted into the characteristic, colourless prisms of (V), m. p. 163°. The *acetyl* derivative crystallised after concentration of the acetic anhydride solution in which it was prepared, and formed colourless rhomboids, m. p. 191° (Found : C, 61·2 ; H, 5·4. $C_{22}H_{22}O_9$ requires C, 61·4 ; H, 5·1%). It is hydrolysed to (VII) by a few moments' treatment with alcoholic potash.

The *compound* of m. p. 154·5° is obtained when the methylation of irigenin is continued for 24 hours or more, with frequent addition of relatively large amounts of alkali and methyl iodide. The excess of methyl iodide and alcohol are distilled off and the substance is precipitated by water, washed with dilute alkali, and crystallised from ethyl alcohol (charcoal), then from benzene, and again from alcohol, being finally obtained in colourless, glistening leaflets, m. p. 154·5°. This substance is devoid of phenolic properties, and is being subjected to further examination.

Alkaline Decomposition of Irigenin 7 : 3'-*Dimethyl Ether*.—Hydrolysis was effected as in the case of irigenin 5 : 3'-dimethyl

ether (below), but twice the quantity of alkali was used and the solution was allowed slowly to become concentrated by distillation. The phenolic and acidic products were isolated as described, and identified as 4 : 5-dimethoxyresorcinol (VIII) and 3 : 4 : 5-trimethoxyphenylacetic acid.

Methylation of Iridin : Irigenin 5 : 3′-Dimethyl Ether (IX).—A freshly prepared, filtered solution of iridin (4 g.) in absolute methyl alcohol (60 c.c.) was treated with diazomethane, prepared from nitrosomethylurethane (16 c.c.) in ether (160 c.c.) and 25% methyl-alcoholic potash (25 c.c.). After 12 hours, the ether was distilled off and the remaining solution treated as before with diazomethane, which still remained in excess after a further 12 hours. After complete evaporation the residue was dissolved in a little water, and the solution was filtered from a slight flocculent precipitate and evaporated to dryness in a vacuum, leaving a yellowish-brown, uncrystallisable resin. This was hydrolysed on the steam-bath with 1% sulphuric acid for 6 hours; crystals were then obtained which separated from methyl alcohol (charcoal) in colourless, silky needles, m. p. 218° (Found*: C, 62·1; H, 5·5; MeO, 36·1. $C_{20}H_{20}O_8$ requires C, 61·8; H, 5·2; 5MeO, 39·9%). *Irigenin 5 : 3′-dimethyl ether* dissolves readily in dilute aqueous sodium hydroxide with a pale yellow colour, and its alcoholic solution gives a very faint brownish colour with ferric chloride. Methylation with metbyl sulphate and alkali readily gave irigenin trimethyl ether (V).

Decomposition of Irigenin 5 : 3′-Dimethyl Ether with Alkali.—The dimethyl ether (0·75 g.) was boiled with water (75 c.c.) in a slow current of hydrogen, and a solution of potassium hydroxide (2·5 g. KOH) added. The colour, at first yellow, rapidly became red and finally faded to a very pale yellow. Decomposition was then probably complete, but boiling was continued for 2 hours, after which the solution was acidified, boiled with charcoal, and filtered. Excess of sodium bicarbonate was now added, and the solution extracted 12 times with ether. The extracts left on evaporation an oil which crystallised completely in a few hours on being kept at about 30°. By recrystallisation from a small amount of benzene, well-formed rhomboids separated (0·17 g.), m. p. 76°, which gave a reddish-brown colour with ferric chloride and had the properties of the 4 : 5-dimethoxyresorcinol recently prepared by Chapman, Perkin, and Robinson (*loc. cit.*). When heated with aqueous sodium hydroxide and chloroform, it develops a bright orange-red colour. Fusion with phthalic anhydride and zinc chloride, followed by treatment with alkali, gives a red solution devoid of fluorescence. The alkaline solution remaining after the

extraction of the 4 : 5-dimethoxyresorcinol was acidified, and the *product then obtained by repeated extractions with ether* crystallised from a small amount of water (charcoal) in colourless, flat needles, m. p. 120°, and had all the properties of 3 : 4 : 5-trimethoxyphenylacetic acid.

The author's thanks are due to the Chemical Society for a grant which has defrayed part of the cost of this investigation.

The Dyson Perrins Laboratory,
Oxford. [*Received, February 3rd*, 1928.]

ANNUAL GENERAL MEETING,

THURSDAY, MARCH 22ND, 1928, AT 4 P.M.

PROFESSOR H. BRERETON BAKER, C.B.E., D.Sc., F.R.S., President, was in the Chair.

The Report of the Council for 1927—1928, together with the Balance Sheets and Statements of Accounts for 1927, was presented, and a statement on the finances of the Society was made by the Treasurer. The adoption of the Report was proposed by Dr. L. J. SPENCER, seconded by Professor J. C. PHILIP, and carried unanimously.

REPORT OF COUNCIL, 1927–1928.

I. *Fellowship Statistics.*

THE number of Fellows at the 31st December, 1926, was 4093. During 1927, 190 Fellows were elected and 10 reinstated, giving the gross total of 4293. The deaths recorded were 40; the resignations numbered 103, and the names of 110 Fellows were removed from the List of Fellows for non-payment of Annual Subscriptions, the corresponding figures for the previous year being 32, 101, and 115, respectively. The number of Fellows, therefore, at the 31st December, 1927, was 4040, showing a decrease of 53 in the membership of the Society.

This decline in the number of Fellows is more than accounted for by the fact that the elections of new Fellows numbered only 190 as against an average of 270 for the past 10 years. The Council views the position with concern, and trusts that Fellows will use their best endeavours to bring before those interested in the advancement of chemical knowledge the advantages offered by the Fellowship of the Chemical Society.

During the year the Society has had to mourn the loss of one of its distinguished Past-Presidents, Dr. Arthur W. Crossley, who was President from 1925 to 1926, relinquishing the office after one year, owing to ill-health. He served on the Council in all for a period of twenty-two years, and a record of his eminent services to Chemistry in general and to the Society in particular is given in the obituary notice prepared by Professor W. P. Wynne appearing in the December Journal. The Council elected Sir William J. Pope as a Vice-President to fill the vacancy caused by Dr. Crossley's death.

The Council has also suffered the loss of its two senior Honorary Fellows, Professor Svante Arrhenius and Professor Ira Remsen,

who were elected on the 20th January, 1898. A memorial lecture to the former will be delivered by Sir James Walker next May, and an obituary notice of Professor Ira Remsen, prepared by Professor W. A. Noyes, appears in the Journal for December. During 1927, Sir Joseph J. Thomson, O.M., and Professor Richard Willstätter were elected Honorary Fellows, the number of whom, therefore, still remains at 23.

The congratulations of the Society have been conveyed to Mr. Oliver Quibell, elected March 4th, 1868, who has completed 60 years of Fellowship, and to the following Fellows who have attained their jubilee as Fellows during the year:

	Elected.
Beeby Thompson	June 21st, 1877.
Frederick Woodland Toms	June 21st, 1877.
Ayerst Henham Hooker	Feb. 7th, 1878.
Frederick Stuart Harris	Feb. 7th, 1878.
Walter Bezant Lowe	Feb. 21st, 1878.
Lewis Thompson Wright	Feb. 21st, 1878.

II. *Publications.*

The Journal for 1927 contains 3205 pages, of which 3096 pages are occupied by 414 memoirs and 28 notes, the remaining 109 pages being devoted to Obituary Notices (43 pages), two Lectures (39 pages), the Report of the General Meeting (17 pages), and the Presidential Address (10 pages). The volume for 1926 contains 3248 pages, of which 3089 are devoted to 437 memoirs and 29 notes.

During 1927, 485 papers were offered to the Society for publication in the Journal; of these, 23 were declined. The corresponding numbers for 1926 were 528 and 35.

The average interval between the dates of receipt and of publication of papers was 10½ weeks for 1927, 14 weeks for 1926, and 13 weeks for 1925.

The Council again records its indebtedness to those Fellows who referee papers.

III. *Library.*

Excluding the evenings on which meetings of the Chemical Society were held, there were 8002 attendances during the past year. Of these, 5408 were made by Fellows of the Chemical Society, and 2594 by members of contributing Societies, compared with 7692 and 2419, respectively, in 1926, while the number of books borrowed during 1927 was 5489 as against 5353 the previous year.

The additions to the Library comprise 286 books, of which 114 were presented, 702 volumes of periodicals (including a gift of 77

volumes from the Faraday Society), and 86 pamphlets; as against 295 books, 593 volumes of periodicals, and 48 pamphlets last year. The Library now contains 31,887 volumes, consisting of 9,647 books and 22,240 bound volumes of periodicals.

IV. *General.*

The Faraday Lecture was delivered by Professor Richard Willstätter at the Royal Institution (by courtesy of the Managers) on May 18th, and the Council decided to issue reprints of the lecture at the price of 1*s*. each. Of two other lectures arranged to take place in the Meeting Room of the Society, the first was given by Professor W. A. Bone, F.R.S., on November 24th, the title of his Lecture being "Gaseous Combustions at High Pressures," and the second, entitled "Spectra and Atoms," was delivered by Professor A. Fowler, on February 23rd.

The President, together with Mr. A. Chaston Chapman and Professor C. S. Gibson, represented the Society at the Berthelot Celebrations held in Paris in September, and an Address of Congratulation was presented by the President at the Séance Solennelle in the Sorbonne; Mr. Chaston Chapman was also the Society's delegate at the 7-ième Congrès de Chimie Industrielle. The President, who was the Society's delegate at the Jubilee Celebrations of the Institute of Chemistry, presented an Address of Congratulation at the Dinner on December 15th, the Ordinary Scientific Meeting fixed for that day having been abandoned.

Professor W. A. Bone acted as the Society's delegate at the Conference on "Methods of Coal Analysis" held in October, and Dr. J. J. Fox agreed to continue to serve on the Aircraft Sub-Committee on Chemicals of the British Engineering Standard Association. Dr. Fox also represents the Society on the New International Association for Testing Materials.

The President has been nominated to serve on the Court of Bristol University in the place of the late Sir William A. Tilden; Dr. V. J. Harding was the Society's delegate at the Annual Convention of Chemists of Canada held in Quebec in June, and Sir William J. Pope has been nominated to serve on the Organising Committee of the 7th International Congress of Photography to take place in London on July 9th to 14th, 1928.

At the Anniversary Dinner on March 24th, at which the company numbered 170, the Society was honoured by the presence of Professor Camille Matignon, representing the French Chemical Society, and Hofrat Professor Dr. W. Schlenk, the President of the German Chemical Society. The Presidents of the Belgian, Danish, Dutch, Finnish, Norwegian, Swedish, and Swiss Chemical Societies have

been invited to be the foreign guests of honour at the next Anniversary Dinner on March 22nd, 1928.

The Council has agreed to co-operate in a joint chemical dinner ;o be held in London in the autumn of 1928, and has appointed the Assistant Secretary to serve on the Committee responsible for the ırrangements.

The Society's representatives on the Bureau of Chemical Abstracts 'or 1928 are Professor C. S. Gibson, Mr. A. J. Greenaway, Dr. J. T. Hewitt, Professor G. T. Morgan, and the Treasurer, who serves as ın *ex-officio* member. The "A" Abstracts for 1927 contained 8010 ıbstracts occupying 1230 pages, compared with the corresponding igures in 1926, of 7978 abstracts occupying 1284 pages, and the ıverage length per abstract was 0·30 of a column as against)·32. The 8010 abstracts comprised 4157 in General, Physical, ınd Inorganic Chemistry, 80 in Mineralogical, 2095 in Organic, and 678 in Bio-chemistry. As from January 1928, the title of 'Mineralogical Chemistry" will be altered to "Geochemistry." 'or the Abstracts for 1928, it has been decided to use a paper 30 per ent. lighter in weight than that previously utilised. A substantial aving in the cost of paper will follow as a result of this change, and t is anticipated that there will be a saving in postage on the "A" Abstracts.

Professor C. S. Gibson, Sir William J. Pope, and Professor J. F. 'horpe continue to represent the Society on the Federal Council, nd Professor A. J. Allmand and Professor F. G. Donnan have een appointed to serve for two years on the Editorial Board of the *ournal of Physical Chemistry*, in the place of Professor J. W. IcBain and Professor J. C. Philip, retired. During 1927, the British Members of the Editorial Board received 26 papers, of 'hich 12 have been published, 10 await publication, and 4 are nder consideration; 12 reviews of books have also been prepared.

Under the will of the late Professor W. Carleton Williams, the ociety is to receive at the death of his daughter the sum of £1000 ›r the maintenance and support of the Society's Journal and ibrary. Further, a bequest of £500 has been made by the late 'rofessor Archibald Liversidge to found a lectureship for the xpress purpose of encouraging research. Accordingly, it has been ecided to create a "Special Lectures Fund" into which the £500 'om Professor Liversidge and an equal amount from the general ınds of the Society will be paid, the income derived from this fund › be devoted to providing honoraria for the lecturers to be appointed y the Council. Two Annual Lectureships have thus been estabshed, one to be designated the "Liversidge Lecture" and the ther the "Pedler Lecture." The lectures will deal as far as

practicable with the description of new knowledge, and the lecturers, who will be selected by reason of their own discoveries, will indicate in their lectures the directions in which further research work is desirable. The lectures will be open to the public free by ticket.

Volume II of the Memorial Lectures has been reproduced by the photolithographic process and can be obtained by Fellows at 7*s*. per copy. It has also been decided to publish in the near future a volume containing the Faraday Lectures delivered before the Society.

The cordial thanks of the Council have been conveyed to Miss Gladstone for presenting an Album containing photographs of eminent Chemists and other Men of Science, which belonged to the late Dr. John Hall Gladstone, Past-President, and to Lady Ramsay for presenting to the Library a number of books from the library of the late Sir William Ramsay. The Council has also gratefully acknowledged gifts of the Society's publications from Mr. Leonard Archbutt, Mr. R. E. Crowther, Mrs. E. D. Gravill, Mr. H. F. Robinson, and Dr. F. K. Viccajee.

The collection of medals has been enriched by replicas of the Horace Brown Medal from the Institute of Brewing and the Amé Pictet Medal struck in commemoration of his seventieth birthday, which was celebrated last November.

The Council has referred to a committee for consideration and report the question of revising the Bye-Laws, such revision being rendered especially necessary by the fact that they contain no provision for the establishment of the Bureau of Chemical Abstracts. The Council hopes shortly to be in a position to submit its recommendations to the Fellows for their consideration.

The List of Fellows corrected up to July 31st was issued in September free of charge to those Fellows who had made application.

During the year, 90 applications for research grants were received from Fellows asking for £960 10*s*., and 9 from non-Fellows asking for £95. 85 grants amounting to £677 10*s*. were made to the former and 3 grants amounting to £20 to the latter. Since the sum applied for each year far exceeds the amount available for distribution, the Council has resolved that in ordinary circumstances, if a grantee incurs no expenditure during two consecutive years while holding the grant, the amount in his hands shall be returned to the Society; also, that any balance remaining in a grantee's hands after he has held the grant for four years shall be returned to the Society.

At the Ordinary Scientific Meeting on June 16th, 1927, the President made a presentation to Mr. S. E. Carr of two cheques,

one from the Council and the other from Fellows, together with an album containing the signatures of the Honorary Fellows and Fellows who had contributed, and a clock, to mark the completion of his 25th year as Assistant Secretary.

The Council again acknowledges its indebtedness to those who have delivered lectures before the Society, to Fellows and others who have prepared obituary notices, and to the authors of the Annual Reports for 1927.

V. *Financial.*

It is gratifying to record that during the year under review the income of the Society has increased by £206 9*s*. 6*d*., whilst the expenditure has decreased by £114 17*s*. 2*d*., and that there is a balance in hand of £456 6*s*. 8*d*.

Income. The chief cause of the increased income is to be found in the contribution from the Publications Fund, which is this year greater by £199 4*s*. 6*d*. than that of last year. There have been increases in the amounts received from Publications sales (£80 18*s*. 11*d*.) and from interest on investments (£49 7*s*. 6*d*.), but the contributions to the Library show a decrease of £101 1*s*.

Expenditure. Compared with 1926, the cost of the Journal has decreased by £14 14*s*. 3*d*., and the Abstracts by £88 16*s*.; this year each account bears its share of the cost of superannuation previously borne by administration expenses, the charges being £37 16*s*. 3*d*. and £9 4*s*. 5*d*. respectively. Administration expenses are less by £323 16*s*., due to a saving under the item of wages of £135 17*s*. 0*d*., of which £82 14*s*. has been charged to the Library Account, and to a saving of £130 6*s*. 10*d*. on miscellaneous printing and stationery. This year, the Accounts have to bear the cost of the List of Fellows (£129 8*s*. 2*d*.) and increased cost of pensions (£94 5*s*.).

Income Tax. It will be noticed that Income Tax, which is deducted at the source from the interest on all the Society's investments excepting 5% War Loan and 5% National War Bonds, and which has been hitherto recovered without question, is, this year, shown under the items "Income tax recovered" and "Income tax recoverable." This action has been rendered necessary by the Inland Revenue Commissioners, who have informed the Council that pending the decision in the High Court of two test cases, they are unable to continue to exempt the Society from paying income tax. The figures shown under "Income tax recovered" represent the tax returned in respect of the income for 1926 up to the 5th April, and those given under the items "Income tax recoverable," amounting in all to £131 0*s*. 6*d*., indicate the sum due in respect of the period 5th April to 31st December, 1926.

General. It is of interest to review the financial position in this the ninth year after the Armistice, in order to see how far financial conditions may be regarded as stabilised. During the war years 1914—1918, the small volume of research work published led to a succession of credit balances amounting in all to some £7000. These accumulated funds, however, were used up during the next five years, notwithstanding the fact that in 1921 the annual subscription was raised from £2 to £3, and it became clear in 1923 that new sources of income would have to be provided and drastic economies exercised. As a result of the action then taken, the accounts for the years 1924—1927 showed credit balances of £210, £466, £135, and £456 respectively, and there is thus reason to hope that a measure of stability in the financial affairs of the Society has been attained.

In this connexion it is to be observed that for 1927, while the number of pages in the Journal shows a decrease of 43 pages compared with 1926, the Abstracts also number 56 pages fewer than in the previous year. If this proves to be a true indication that the increase in expenditure on account of its publications, which the Society has had to face since the war, is ceasing, then it may be possible that the Council will be able in the near future to relax some of the restrictions that have had to be enforced.

Publications Fund. The Fund has now been established for four years, and, thanks to the benefaction from the late Sir Alexander Pedler and to donations from Fellows and manufacturers, the capital sum now stands at £10,375 0*s.* 4*d.* This year the fund contributed £961 0*s.* 8*d.* to the General Fund, but £350 of this was again derived from the Government Publications Grant administered by the Royal Society, for which the Council desires to express its thanks. The Publications Fund will continue automatically to increase by the yearly sums paid as Life Composition Fees and, it is hoped, will be augmented by further contributions and legacies.

Special Publications Fund.

The sales of the various publications financed by means of this fund have realised £238 2*s.* 9*d.* towards the total cost of £401 13*s.* 4*d.* incurred in publication, and there is reason to anticipate that in time the various ventures will pay for themselves.

Miscellaneous.

As in former years, the Society has again contributed £100 towards the expenses of the Federal Council. For the first time, the accounts of the Bureau of Chemical Abstracts are included with those of the Society, the Council considering that as the Society is responsible for approximately one-half of the expenditure incurred

by the Bureau, its accounts should be submitted to the Fellows. The expenses incurred on account of Abstracts "A" (Pure) are incorporated in the varions items appearing in the Chemical Society's Income and Expenditure Account under the heading "Expenses on account of Abstracts." The figures are arrived at as follows:

Salaries, £472 10*s*. (half common) + £414 (Pure) + £214 7*s*. 11*d*. (Index) = £1100 17*s*. 11*d*.

Postages, £18 7*s*. 11*d*. (half common) + £25 17*s*. 10*d*. (Pure) = £44 5*s*. 9*d*.

Abstractors' fees, £1162 17*s*. 7*d*. (Pure).

Abstracts Index, £665 13*s*. 8*d*. (Printing) + £2 16*s*. 2*d*. (Banding) + £14 18*s*. 8*d*. (Distribution), (total £683 8*s*. 6*d*.).

Miscellaneous, £8 2*s*. 8*d*. (Stationery, half common) + £6 9*s*. 6*d*. (Journals, half common) + £1 1*s*. 8*d*. (Travelling, half common) + £4 19*s*. 4*d*. (Travelling, Pure) + £20 11*s*. 4*d*. (General expenses, half common) = £41 4*s*. 6*d*.

During the year the Bureau, after receiving expert advice, decided to use a lighter paper for its publications, the change to commence with the January 1928 issue. The advantages seemed so considerable that the Council decided to use the same paper for the Journal, and by an arrangement with the printers it was found possible to effect the change in January of this year. It is considered that not only will the Fellows henefit by having a Journal which for the full year will weigh ahout 3 lb. less than hitherto and be 2 inches less in thickness, hut the Society will save approximately £250 on postages and paper.

The Council has to thank Dr. D. S. Jerdan for a contribution of £15 in augmentation of his Life Composition Fee.

A vote of thanks to the Auditors (Dr. O. L. Brady, Dr. A. E. Dunstan, and Dr. G. W. Monier-Williams) for their services, proposed by the TREASURER, and seconded by Mr. R. L. COLLETT, was carried unanimously, Dr. G. W. MONIER-WILLIAMS making acknowledgment. On the proposal of Professor J. R. PARTINGTON, seconded by Dr. A. BRAMLEY, Dr. Brady, Dr. Dunstan, and Dr. Monier-Williams were unanimously elected Auditors to audit the Accounts of the Society for 1928.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council, and Committees for their services during the past year, proposed hy Professor A. G. PERKIN, and seconded by Dr. J. J. SUDBOROUGH, was carried unanimously, and acknowledged by Professor W. P. WYNNE.

The PRESIDENT then delivered his Address, entitled, "Constitu-

tion of Liquids. Some New Experiments." A vote of thanks to the PRESIDENT for his services in the Chair during the past year and for his Address, was proposed by Professor H. E. ARMSTRONG seconded by Sir ROBERT ROBERTSON, and carried unanimously, the PRESIDENT making acknowledgment.

The report on the election to vacancies on the Council for the year 1928—1929 was read as follows:

President.—Jocelyn F. Thorpe.

Treasurer.—T. Slater Price.

Secretary.—T. S. Moore.

Vice-Presidents who have filled the office of President.—H. Brereton Baker, W. H. Perkin, Sir William J. Pope, Sir James Walker.

Vice-Presidents who have not filled the office of President.—W. H. Mills, J. C. Philip.

Ordinary Members of Council.—

Town Members.—W. A. Bone, H. King, J. L. Simonsen, S. Sugden, H. Terrey, Miss M. A. Whiteley.

Country Members.—W. M. Cumming, N. V. Sidgwick.

Professor J. F. THORPE then took the Chair and declared the meeting closed.

	£ s. d.	£ s. d.	£ s. d.
Common...		945 0 0	
Applied		396 0 0	
Pure		414 0 0	
			1755 0 0
„ Abstractors:			
Applied		885 15 11	
Pure		1162 17 7	
			2048 13 6
„ Printing and Stationery:			
Common			16 5 3
„ Sundry Journals			12 18 11
„ Postages:			
Common...		36 15 11	
Pure...		25 17 10	
			62 13 9
„ Travelling:			
Common...		2 8 4	
Applied		14 0 8	
Pure...		4 19 4	
			21 8 4
„ Index:			
Applied			
Remuneration	61 9 8		
Printing	925 13 4		
		987 3 0	
Pure			
Remuneration	214 7 11		
Printing	683 8 6	897 16 5	
			1884 19 5
„ General Expenses:			
Common...		41 2 9	
Applied		1 18 0	
			43 0 9
			£5844 14 11

	£ s. d.
By Society of Chemical Industry	2812 0 8
„ Chemical Society	3032 14 3
	£5844 14 11

Balance Sheet as at 31st December, 1927.

Liabilities.	£ s. d.	£ s. d.
Sundry Creditors:		
Society of Chemical Industry	69 8 9	
Chemical Society...	89 17 9	
Sundry Journals	1 15 0	
Auditors	5 5 0	
		166 6 6
		£166 6 6

Assets.	£ s. d.	£ s. d.
Cash at Bank	158 8 3	
Cash in Hand	7 18 3	
		166 6 6
		£166 6 6

We report that we have examined the above Balance Sheet with the Books and Vouchers of the Bureau and, having obtained all the information and explanations we have required, we are of opinion that such Balance Sheet is properly drawn up so as to exhibit a true and correct view of the state of the Bureau's affairs according to the

INCOME AND EXPENDITURE AC

1926 £ s. d.	1926 £ s. d.	*Income.*	1! £ s. d.
	190 10 0	To Life Compositions	
		,, Annual Subscriptions :—	
1054 10 0		Received in advance, on account of 1927	942 0 0
8318 10 0		,, during 1927 ,, ,, ...	8397 3 0
497 12 0		,, ,, ,, ,, 1926	524 0 0
39 8 0		,, ,, ,, ,, 1925 and previous years	46 2 0
9910 0 0			9909 5 0
500 0 0		*Less* amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	500 0 0
9410 0 0			9409 5 0
500 0 0	9910 0 0	*Add* Arrears at date: £897 17*s.*; Estimated to realise as per Balance Sheet	500 0 0
		,, Investments, Dividends on :—	
25 3 10		£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	25 3 10
36 10 0		£1520 14*s.* 8*d.* Cardiff Corporation 3 per cent. Stock, 1914/54	36 10 0
35 0 0		£1400 India 2½ per cent. Stock	31 10 0
48 0 0		£2400 Bristol Corporation 2½ per cent. Debenture Stock	48 0 0
86 16 4		£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	86 16 4
28 16 0		£1200 Leeds Corporation 3 per cent. Stock	28 16 0
45 0 0		£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53 ...	40 10 0
28 16 0		£1200 London and North Eastern Railway 3 per cent. Debenture Stock	28 16 0
19 12 0		£700 Canada 3½ per cent. Stock, 1930/50	19 12 0
105 0 0		£2100 5 per cent. War Stock, 1929/47	105 0 0
44 0 0		*£1100 5 per cent. War Bonds, 1929/47*	44 0 0
24 0 0		£600 Funding Loan, 4 per cent., 1960/90	21 12 0
332 9 0		£11873 3½ per cent. Conversion Stock	332 9 0
114 0 0		,, Income Tax recovered	69 15 8
—		,, Income Tax recoverable	92 15 8
55 7 10	1028 11 0	,, *Interest on Deposit*	96 12 10
		,, Publication Sales :—	
2631 7 11		Journals and Proceedings	2765 11 11
2438 12 11		Abstracts	2336 2 2
113 10 4		Collective Index, Vols. I–VI	118 5 5
767 1 11		Annual Reports on Progress of Chemistry	820 19 8
27 9 0		Memorial Lectures. Vol. II.	15 8 3
9 4		Other Publications	9 6
5978 11 5			6056 16 11
546 9 9	5432 1 8	*Less Publishers' Commission*	543 16 4
538 1 5		,, Proceeds of Advertisements in Journal and Abstracts ...	548 12 9
148 1 9	389 19 8	*Less* Commission	153 14 1
	60 1 5	,, Miscellaneous Receipts...	
	682 16 0	,, Contributions to Library	
		,, Transfer from Publications Fund, viz.:—	
350 0 0		Government Publications Grant (through the Royal Society)	350 0 0
325 18 2		Dividends and Interest on Deposit	531 18 2
85 18 0	761 16 2	Subscriptions	79 2 6
	£18,455 15 11		£1
	148 19 4	To Pedler Bequest, Balance of Income from Residue of Estate of Sir Alexander Pedler	
	1800 0 0	,, *Pedler Bequest, Balance of Capital	
	421 0 0	,, Excess of extraordinary Expenditure over extraordinary Income, carried to Balance Sheet	
	£2,384 19 4		£

...R THE YEAR ENDED 31ST DECEMBER 1927.

1926 £ s. d.	1926 £ s. d.	Expenditure.	1927 £ s. d.	1927 £ s.
		By Expenses on account of Journal :—		
35 7 0		Editorial Salaries ...	1020 15 0	
38 5 1		Editorial Postages ...	63 15 11	
73 7 1		Printing of Journal ...	3635 14 6	
58 11 4		Banding ...	85 18 3	
73 12 7		Printing of Advertisements ...	77 16 6	
5 9 9		Addressograph Labels ...	5 3 5	
10 7 11		Distribution of Journal ...	529 7 0	
36 14 3		Authors' Copies ...	320 11 9	
5 5 0		Insurance of Stock ...	5 5 0	
17 11		Warehousing of Stock ...	—	
—		Superannuation of Staff ...	37 16 3	
0 16 11		Miscellaneous ...	10 13 3	
	5769 14 10			5702 16
		,, Expenses on account of Abstracts :—		
30 15 0		Editorial Salaries (Bureau) ...	1100 17 11	
39 16 11		Editorial Postages (Bureau) ...	44 5 9	
44 11 6		Abstractors' Fees (Bureau) ...	1162 17 7	
72 5 3		Printing of Abstracts (Bureau £665 13s. 8d.) ...	3061 1 0	
58 11 4		Banding (Bureau £2 16s. 2d. ...	85 18 2	
5 9 8		Addressograph Labels ...	5 3 5	
10 8 0		Distribution of Abstracts (Bureau £14 18s. 8d.) ...	529 7 1	
5 5 0		Insurance of Stock ...	5 5 0	
17 10		Warehousing of Stock ...	—	
—		*Superannuation of Staff* ...	9 4 5	
55 15 11		Miscellaneous (Bureau) ...	41 4 6	
	6124 16 5			6045 4
	36 14 8	,, Lecture Expenses ...		56 1
	90 12 7	,, Advance Proofs and Reports of Meetings ...		92 17
	635 19 3	,, Annual Reports on the Progress of Chemistry ...		587 1
	40 8 10	,, Purchase of Back Numbers of Publications... ...		9 1
	—	,, List of Fellows—Printing, etc.... ...		129 8
	2093 11 6	,, Library Expenses ...		2217 1
		,, Donations :—		
10 10 0		Optical Convention ...	—	
00 0 0		Federal Council ...	100 0 0	
	110 10 0			100
		,, Administration Expenses :—		
30 13 6		Salaries of Staff ...	1444 2 0	
12 14 6		Wages (Commissionaire, Housekeeper, and Charwomen)	276 17 6	
57 4 1		Coal and Lighting ...	66 12 11	
53 2 10		House Expenses and Repairs ...	187 19 5	
73 3 4		Furniture ...	1 12 6	
22 16 0		Telephone ...	19 9 5	
44 4 7		Tea Expenses ...	34 5 4	
24 16 4		Insurances ...	13 5 0	
31 10 0		Accountants' Charges ...	31 10 0	
—		Ditto Pedler Bequest ...	45 0 0	
5 14 0		Commission on Recovery of Income Tax ...	3 0 9	
46 16 0		Miscellaneous Printing and Stationery ...	316 0 2	
56 6 8		Postages ...	141 14 5	
35 0 7		Expenses at Annual General Meeting ...	42 18 2	
76 5 2		Superannuation of Staff ...	128 0 1	
19 2 0		Addresses ...	12 18 0	
91 13 3		Miscellaneous Expenses ...	86 3 2	
	8176 2 10			2852
	190 10 0	,, Transfer to Publications Fund (Life Composition Fees) ...		175 1
	51 15 0	,, Staff Pensions Fund—Pensions paid during 1927 ...		146
	135 0 0	,, Excess of ordinary Income over ordinary Expenditure carried to Balance Sheet ...		456
	£18,455 15 11			£18,662
	143 19 4	By Publications Fund—Income from Pedler Bequest ...		102
	1800 0 0	,, Publications Fund—Capital from Pedler Bequest ...		2985 1
	200 0 0	,, Staff Pensions Fund, transferred from accumulation of General Purposes Account at 31st December, 1925 ...		—
	221 0 0	,, Cost of New Library Bookshelves ...		—
	£2,[illegible] 4			£3,068

Income and Expenditure Accounts of other Funds for the Year ended 31st December, 1927.

RESEARCH FUND.

1926 £ s. d.	*Income.*	1927 £ s. d.	1927 £ s. d.
	To Dividends on :		
32 0 0	£1000 *London and North Eastern* Railway 4 per cent. 2nd Guaranteed Stock ...	32 0 0	
20 13 8	£1034 Great Western Railway 2½ per cent. Stock	20 13 8	
84 5 8	£1142 16s. New South Wales 3 per cent. Stock	30 7 2	
33 13 2	£1122 Metropolitan Water Board 3 per cent. "B" Stock	30 5 11	
27 5 10	£1483 London, Midland and Scottish Railway 4 per cent. Debenture Stock	27 5 10	
19 6 10	£806 Victoria 3 per cent. Stock, 1929/49	19 6 10	
224 18 6	£4498 11*s*. 0*d*. 5% War Loan, 1929/47 ..	224 18 6	
180 15 2	£5164 18*s*. 9*d*. 3½% Conversion Stock ..	163 3 8	
			548 1 7
27 0 0	,, *Income Tax Recovered*		12 8 3
—	,, Income Tax Recoverable		12 8 3
180 15 0	,, Repayment of Grants		137 18 0
15 19 6	,, Interest on Deposit		8 7 7
81 16 5	,, Sale of Apparatus		1 15 4
—	,, Balance, being *Excess of Expenditure over* Income, carried to Balance Sheet		5 3 11
£828 9 9			£726 2 11

1926 £ s. d.	*Expenditure.*	1927 £ s. d.	1927 £ s. d.
772 0 0	By Grants		697 10 0
1 7 0	,, Commission on Recovery of Income Tax...		12 5
6 19 0	,, Advertisements, etc.		8 0 6
21 0 0	,, Honorarium to Lecturer		20 0 0
27 3 9	,, Balance, being Excess of Income over Expenditure, carried to Balance Sheet ...		—
£828 9 9			£726 2 11

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

1926 £ s. d.	Income	1927 £ s. d.	1927 £ s. d.
	To Dividends on :—		
25 0 0	£500 National War Bonds, 5%, 1928 ...	25 0 0	
25 0 0	£500 National War Bonds 5%, 1929 ...	25 0 0	
2 3 2	£61 15*s*. 8*d* Conversion Stock, 3½% ...	2 3 2	
3 9 9	Interest on Deposit	1 13 5	
			53 16 7
84 12 2	,, Balance, being Excess of Expenditure over Income, carried to Balance Sheet		102 18 5
[illegible]			[illegible]

1926 £ s. d.	Expenditure	1927 £ s. d.
5 4 6	By Advertisements	—
135 0 0	,, *Cost of Plaque*..	6 15 0
—	,, Prize	150 0 0
[illegible]		[illegible]

£ s. d.		£ s. d.	£ s. d.
190 10 0	To Transfer from General Account, being Life *Composition Fees for year* ...		175 10 0
99 0 0	,, Subscriptions ...		85 3 6
1102 0 0	,, Donations ...		25 0 0
350 0 0	,, Government Publications Grant (through the Royal Society) ...		350 0 0
152 8 6	,, Dividend on £5,933 10*s.* 2*d.* Conversion Stock, 3½ per cent. ...	168 0 0	
24 11 4	,, Ditto £3,079 3*s.* 9*d.* War Stock, 5%, 1929/47	153 19 2	
—	,, Ditto £710 P. & O. Steam Navigation Co. Deferred Shares...	71 0 0	
—	,, Ditto 186 £1 Shares Lungla (Sylhet) Tea Co.	7 13 5	
—	,, Ditto 124 £1 Shares Nedeem Tea Co. ...	25 5 3	
148 19 4	,, Balance of Income from Pedler Bequest, transferred from General Account ...	102 7 10	
4 10 0	,, Interest on Deposit ...	3 3 6	531 18 2
9 4 3	,, Income Tax recovered ...	13 17 3	
—	,, Income Tax recoverable ...	18 9 0	32 6 3
1800 0 0	,, Balance of Capital from Pedler Bequest, transferred from General Account ...		2985 16 2
£3877 1 10			£4185 14 1

£ s. d.		£ s. d.	£ s. d.
	By Transfer to General Account—Income applicable to 1927 Publications, viz.:—		
350 0 0	,, Government Publications Grant (through the Royal Society) ...	350 0 0	
85 18 0	,, Subscriptions ...	79 2 6	
325 18 2	,, Dividends and Interest on Deposit ...	531 18 2	961 0 8
9 3	,, Commission on recovery of Income Tax ...		13 10
13 2 0	,, Subscriptions in advance (carried forward)		0 7 0
	,, Balance, being excess of Income over Expenditure, carried to Balance Sheet, viz :—		
190 10 0	,, Life Composition Fees ...	175 10 0	
8 15 5	,, Income Tax recovered (net) ...	31 12 5	
1102 0 0	,, *Donations* ...	25 0 0	
1800 0 0	,, Balance of Capital from Pedler Bequest ...	2985 16 2	3217 18 7
£3877 1 10			£4185 14 1

SPECIAL PUBLICATIONS FUND.

£ s. d.		£ s. d.	£ s. d.
43 2 0	To Sales:—Memorial Lectures, Vol. I ...	34 5 0	
72 3 11	Portraits ...	44 1 10	
—	Faraday Lecture ...	3 1 3	
115 5 11		81 8 1	
4 16 11	*Less* Commission ...	6 4 4	
110 9 0			75 3 9
59 4 8	,, Dividend on £2115 8*s.* 10*d.* Conv. Stock, 3½%		59 4 8
9	,, Interest on Deposit...		3 8 10
—	,, Income Tax recovered ...		7 8 0
—	,, Income Tax recoverable ...		7 8 0
19 8 1	,, Balance, being Excess of *Expenditure* over Income carried to Balance Sheet ...		—
£189 2 6			£152 13 3

£ s. d.		£ s. d.
	By Cost of Reproduction:—	
171 14 10	Printing Portraits of Eminent Chemists	—
—	Faraday Lectures ...	4 15 6
17 6 6	,, Advertising ...	3 3 0
—	,, Commission on recovery of Income Tax ...	7 5
1 2	,, Miscellaneous Expenses ...	—
—	,, Balance, being excess of Income over Expenditure carried to Balance Sheet...	144 7 4
£189 2 6		£152 13 3

STAFF PENSIONS FUND.

£ s. d.		£ s. d.
200 0 0	To Transfer from General Account (from accumulation of Funds) ...	—
51 15 0	,, Transfer from General Account (to meet pensions for current year) ...	146 0 0
[illegible]	Donations	5 5 0

£ s. d.		£ s. d.
51 15 0	By Pensions paid during 1927 ...	146 0 0
362 0 11	,, Excess of Income over Expenditure carried to Balance Sheet ...	23 16 10

1926 £ s. d.	*Income.*	1927 £ s. d.	£ s. d.
	To Contributions:—		
250 0 0	Association of British Chemical Manufacturers	150 0 0	
10 10 0	Biochemical Society	10 10 0	
5 5 0	Faraday Society	5 5 0	
45 0 0	Institute of Brewing	45 0 0	
250 0 0	Institute of Chemistry	250 0 0	
100 0 0	Society of Chemical Industry	100 0 0	
10 10 0	Society of Dyers and Colourists	10 10 0	
10 10 0	Society of Public Analysts	10 10 0	
1 1 0	Jones, J. P.	—	
			581 15 0
1410 15 6	,, Contribution from General Fund		1636 0 6
£2093 11 6			£2217 15 6

1926 £ s. d.	*Expenditure.*	1927 £ s. d.	£ s. d.
1222 17 6	By Salaries and Wages...		1295 10 0
88 15 0	,, Superannuation of Staff		93 11 9
526 11 4	,, Books and Periodicals		491 18 7
128 12 9	,, Binding		140 15 9
42 2 4	,, Printing, Stationery and Postage		73 11 0
79 7 4	,, Lighting, Heating, Furniture, & Insurance		105 0 5
5 5 3	,, Miscellaneous		17 19 0
£2098 11 6			£2217 15 6

THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31st December, 1927.

GENERAL PURPOSES.

£ s. d.	*Liabilities.*	£ s. d.	£ s. d.
942 0 0	To Subs. received in advance:— at £3 0 0 ...		912 0 0
2,221 10 7	,, Sundry Creditors (Printing and other Expenses)		2,850 10 1
464 9 8	,, Bankers—overdraft		75 15 3
26,129 10 8	,, Excess of Assets over Liabilities as per last Balance Sheet	25,840 10 8	
185 0 0	*Add* Excess of Income over Expenditure for Year	456 6 8	
29,889 10 11		26,296 17 4	
421 0 0	*Less* Excess of extraordinary Expenditure over extraordinary Income for Year	—	
			26,296 17 4

£ s. d.	*Assets.*	£ s. d.	£ s. d.
	By *Investments* (value when acquired):—		
839 3 7	£757 London, Midland and Scottish Railway 4 cent. Debenture Stock ...	839 3 7	
1650 0 0	£1520 14s. 3d. Cardiff Corpn. 3% Stock	1650 0 0	
1316 1 0	£1400 India 2½ per cent Stock	1316 1 0	
2070 2 0	£2400 Bristol Corpn. 2½% Debenture Stock, Bristol Dock Account	2070 2 0	
3572 0 4	£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	3572 0 4	
1143 1 0	£1200 Leeds Corporation 3% Stock ...	1143 1 0	
1460 13 6	£1500 Transvaal 3 per cent. Guaranteed Stock, 1923–53	1460 13 6	
1033 11 0	£1200 London and North Eastern Railway 3 per cent. Debenture Stock	1033 11 0	
704 8 6	£700 Canada 3½% Stock, 1930/50 ...	704 8 6	
1995 0 0	£2100 5 per cent. War Stock, 1929/47...	1995 0 0	
1045 0 2	£1100 5% National War Bonds, 1929/47	1045 0 2	
480 0 0	£600 4 per cent. Funding Loan, 1960/90	480 0 0	
8987 2 2	£11,873 3½ per cent. Conversion Stock (Market Value £22,051 11s. 2d.)	8987 2 2	
			26,296 3 8
2617 19 9	,, Sundry Debtors...		2,798 9 8
500 0 0	,, Subscriptions in Arrear £897 17s. Estimated to realise		500 0 0

£ s. d.		£ s. d.	£ s. d.	£ s. d.		£ s. d.	£ s. d.
14,444 12 6	To Excess of Assets over Liabilities as per last Balance Sheet	14,471 16 3			By Investments (value when acquired):		
27 3 9	*Add* Excess of Income over Expenditure for Year	—		1010 0 0	£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed Stock	1010 0 0	
	Less Excess of Expenditure over Income for Year	5 3 11	14,466 12 4	1049 15 11	£1034 Gt. West. Rly. 2½% Debentures	1049 15 11	
				1000 0 0	£1142 16s. 0d. New South Wales 3 per cent. Stock 1935	1000 0 0	
				1002 10 9	£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002 16 9	
				1009 18 9	£1483 London, Midland and Scottish Railway 4% Debenture Stock ...	1508 3 6	
				706 6 2	£806 Victoria 3% Stock, 1929/49 ...	706 6 2	
				4267 4 10	£4498 11s. 0d. 5% War Stock, 1929/47	4267 4 10	
				3898 14 10	£5164 13s. 9d. 3½% Conversion Stock (Market Value £13,271 6s. 7d.)	3898 14 10	14,448 2 0
				—	,, Sundry Debtors		12 8 3
				26 19 0	,, Cash at Bank ... Current Account		1 2 1
				500 0 0	Do. ... Deposit Account		—
£14,471 16 3			£14,466 12 4	£14,471 16 3			£14,466 12 4

THE EDWARD FRANK HARRISON MEMORIAL TRUST

£ s. d.		£ s. d.	£ s. d.	£ s. d.		£ s. d.	£ s. d.
1305 14 11	To Excess of Assets over Liabilities as per last Balance Sheet	1221 2 9			By Investments (value when acquired):—		
84 12 2	*Less* Excess of Expenditure over Income for Year	102 18 5	1118 4 4	500 0 0	£500 National War Bonds 5 per cent. 1928	500 0 0	
				500 0 0	£500 National War Bonds 5 per cent. 1929	500 0 0	
				50 1 5	£61 15s. 8d. 3½ per cent. Conversion Stock (Market Value £1105 1s. 5d.)	50 1 5	1050 1 5
				71 1 4	Cash at Bank .. ... Current Account	28 2 11	
				100 0 0	Do. ... . Deposit Account	40 0 0	68 2 11
£1221 2 9			£1118 4 4	£1221 2 9			£1118 4 4

PUBLICATIONS FUND

£ s. d.		£ s. d.	£ s. d.	£ s. d.		£ s. d.	£ s. d.
13 2 0	To Subscriptions received in advance ...		6 1 0		By Investments (value when acquired):—		
4055 7 4	,, Excess of Assets over Liabilities as per last Balance Sheet	7157 1 9		4500 0 0	£5933 10s. 2d. 3½% Conversion Stock ...	4500 0 0	
3101 14 5	*Add* Excess of Income over Expenditure for Year	3217 18 7	10375 0 4	2300 0 0	£3079 3s. 9d. 5% War Loan 1929/47 ...	3100 0 0	
					£710 P. & O. Steam Navigation Co. Deferred Stock	1846 0 0	
					186 Ordinary Shares (£1) Lungla (Sylhet) Tea Co.	290 12 6	
					124 Ordinary Shares (£1) Nedeem Tea Co. (Market Value £10,205 9s. 6d.)	403 0 0	10,139 12 0
					,, Paid up on £107 P. & O Steam Navigation Deferred Stock		64 4 0
					,, Sundry Debtors		18 9 0
				370 3 9	,, Cash at Bank...		158 15 10
£7170 3 9			£10,381 1 4	£7170 3 9			£10,381 1 4

SPECIAL PUBLICATIONS FUND

1926 £ s. d.	Liabilities.	1927 £ s. d.	1927 £ s. d.
—	To Amounts prepaid for 1928		23 0 0
—	,, Sundry Creditors...		3 3 0
1728 15 4	,, Excess of Assets over Liabilities as per last Balance Sheet	1704 7 3	—
19 8 1	*Less* Excess of Expenditure over Income to 31st December, 1926	—	
		1704 7 3	
—	*Add* Excess of Income over Expenditure to 31st December, 1927	144 7 4	
			1848 14 7
£1704 7 3			£1874 17 7

1926 £ s. d.	Assets.	1927 £ s. d.	1927 £ s. d.
	By Investment :—		
1600 0 0	£2115 8s. 10*d.* 3½% Conversion Stock .. (Market Value £1628 17s. 10*d.*)		1600 0 0
43 12 6	,, Sundry Debtors		63 7 0
10 14 9	,, Cash at Bank ... ... Current Account	61 10 7	
50 0 0	Do. ... ... Deposit Account	150 0 0	
			211 10 7
£1704 7 3			£1874 17 7

STAFF PENSIONS FUND

1926 £ s. d.	Liabilities.	1927 £ s. d.	1927 £ s. d.
—	To Excess of Income over Expenditure		—
15 15 0	,, Excess of Assets over Liabilities as per last Balance Sheet	377 15 11	
362 0 11	*Add* Excess of Income over Expenditure for year...	23 16 10	
			401 12 9
£377 15 11			£401 12 9

1926 £ s. d.	Assets.	1927 £ s. d.	1927 £ s. d.
375 0 0	*By Investment* £371 17*s.* 1*d.* War Stock 5% 1929/47 (Market Value £376 10*s.* 1*d.*) ...		375 0 0
2 15 11	,, Cash at Bank		26 12 9
£377 15 11			£401 12 9

I have examined the above Balance Sheets and accompanying Income and Expenditure Accounts with the Books and Vouchers of the Society, and certify them to be in accordance therewith. I have also verified the Balances at the Bankers and the Investments.

W. B. KEEN,
Chartered Accountant

23, Queen Victoria Street, E.C. 4.
February 10th, 1928.

Approved { G. W. MONIER-WILLIAMS,
A. E. DUNSTAN,
OSCAR L. BRADY.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 22nd, 1928.

By H. BRERETON BAKER, C.B.E., D.Sc., F.R.S.

Constitution of Liquids: Some New Experiments.

LAST year I had the honour of presenting to the Society an address in which an account was given of experiments on the effect of catalysts on the molecular association of liquids. It was shown that these catalysts modified the union of the molecules of liquids, in the same way as they modify ordinary chemical actions. The inference was drawn that in liquids an equilibrium, depending on the temperature and the nature of the liquid, is established between the association and dissociation of molecules, which can be disturbed by the presence of catalysts. I propose in what follows to give an account of experiments which have been in progress during the last few years, extending our knowledge of dried liquids, and, secondly, of experiments which seem to indicate the reason for the great changes which take place in liquids when moisture is removed as completely as possible.

In the first place, a number of determinations of the density of the vapours of dried liquids have been made. The liquid was sealed up with purified phosphorus pentoxide in a tube to which was joined a capillary tube in which a series of ten or twelve bulbs, of about 1·5 c.c. capacity, was blown. The liquid was frozen in liquid air and the whole exhausted. From time to time, as the drying progressed, liquid was distilled into the end bulb, which was then sealed off and used for a determination of vapour density by the method of Victor Meyer, the apparatus being modified as described in a paper on gaseous nitrogen trioxide (J., 1907, **91**, 1865). The following results were obtained:

Substance.	Time of drying (years).	Temp. of detern.	Mol. wt.	Normal mol. wt.
Bromine	2	86°	234·3	160
,,	3	93	242·4	,,
Carbon disulphide	2	90	127·0	76
,, ,,	4	90	137·4	,,
Carbon tetrachloride	3	100	191	154
,, ,,	5	100	201	,,
Ethyl ether	5	102	173·1	74
Methyl alcohol	5	103	90·6	32
n-Hexane	4	100	160·5	86
Benzene	3	100	102·4	78
,,	5	100	125·9	,,
Nitrogen tetroxide	10 + 1	80	101·9	92
,, ,,	10 + 5	40	130·7	,,

The molecular aggregation of the main mass of the liquid is probably greater than is represented by the vapour density, since, as was shown in 1924, fractional distillation of the dried liquid takes place. If it were possible to distil most of the liquid away and then seal up a bulb containing the last fraction, the vapour density would probably show a much higher value.

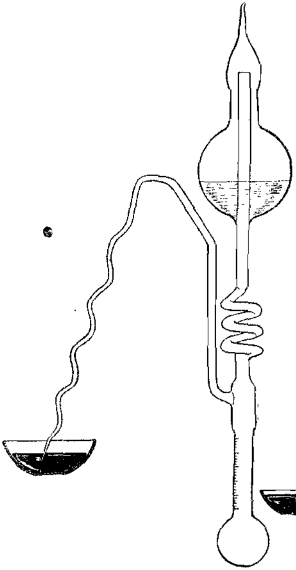


Fig. 1.

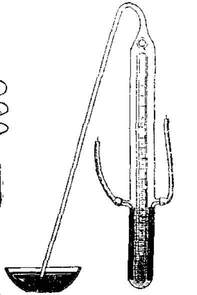


Fig. 3.

It was thought that if association takes place in a dry liquid there must be a change in the latent heat of evaporation. This determination presents peculiar difficulties, since the liquid must not come into contact with the atmosphere. A modification of Berthelot's method was employed, which will be understood from the diagram (Fig. 1). Benzene, carefully purified and distilled from phosphorus

pentoxide, was contained together with phosphorus pentoxide in the upper bulb. After standing for 3½ years, it was distilled by means of a ring burner, into the lower graduated tube, immersed in a known weight of water contained in a Dewar vessel. The boiling point of the liquid was then determined. From the volume of liquid distilled and the rise in temperature of the water, the latent heat of evaporation could be calculated. Two experiments were made with two different pieces of apparatus. The latent heats for 1 gram of benzene were 57·2 and 58, respectively, instead of 83, the normal value. The boiling point of the dried benzene was 94°, and to bring this into conformity with Trouton's rule the molecular weight of the benzene must be 136 instead of 78.

We have, therefore, in favour of the view I have repeatedly expressed, that the removal of water from liquids leads to increased molecular complexity, four separate classes of experimental data: (1) Increase of boiling point, (2) change of surface tension (J., 1922, **121**, 568), (3) increase of vapour density, and (4) for one liquid, decrease in latent heat of evaporation.

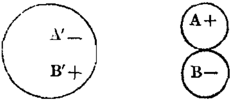


FIG. 2.

As to the reason why the withdrawal of water should bring about the displacement of equilibrium in the direction of larger molecules, there is only one hypothesis, that of Sir J. J. Thomson (*Phil. Mag.*, 1893, **36**, 320), which offers a reasonable explanation of the phenomenon.

Imagine a molecule AB, the atoms of which are held together by electrical attraction (Fig. 2). If a drop of a liquid, with high specific inductive capacity, were adjacent to it, charges would be induced in the drop and the attraction of the atom A to the atom B would be lessened. Therefore the molecule would be more easily dissociated. In the presence of liquid drops of water, therefore, molecules should be less stable. We do not know how many molecules are required to form an effective drop, but single molecules of water would probably not serve. It has been demonstrated by C. T. R. Wilson that the presence of ions in a gas determines the condensation on them of water vapour to form liquid drops. It would seem, therefore, that if we could increase the amount of ionisation in the presence of a small quantity of water vapour, we ought to get a number of drops formed and a decrease in the stability

of the surrounding molecules. In the case of gases which can react, the atoms of their molecules should be less firmly held together and reaction between the gases should be increased. This deduction has been tested as follows. It is known that ionisation is produced in a gas by heated lime, more by thoria, and most, of course, by radium bromide. Silica tubes containing a mixture of hydrogen with nitrous oxide, dried to such an extent that the moisture content was only a few milligrams to a million litres, were heated in a resistance furnace in pairs. One tube contained lime and the other powdered Jena glass. When the combining point was reached, the rate of union in the lime tube was five times that in the tube containing the powdered glass. Another tube containing thoria in place of the lime gave a rate of union twenty times that in the tube with glass alone. After 15 minutes' heating, when a large amount of water had been formed in the reaction, the rate of union became the same, whether powdered glass, lime, or thoria was present. In a third experiment, 2 milligrams of radium bromide were used, and as soon as the combining temperature of the gases was reached the mixture exploded and the tube burst. Thus, increasing the ionisation produced a greater rate of reaction, as we should expect if the formation of liquid drops assisted chemical union.

It has been shown that, in absence of water, liquids are associated, even those, such as hexane and benzene, which are ordinarily taken to be typical non-associated liquids. In my address of last year the condition of all liquids was compared to the gas nitrogen tetroxide, which only at $-20°$ consists entirely of N_2O_4 molecules. Above this temperature we conceive of the gas as a mixture of NO_2 molecules and unaltered N_2O_4 molecules. It is probable that a perpetual dissociation and recombination is taking place, equilibrium changing with temperature. The condition of the molecules in liquids is probably the same, some liquids tending to contain more of the large molecules, such as water and acetic acid, and some less, such as the two liquids mentioned above. In absence of water the large molecules are stable. If the theory outlined above is true, we ought to be able, even in presence of water, but in absence of facilities for its condensation into drops, to stabilise the large molecules and increase the number of them above the normal number corresponding to a given temperature. This I have attempted to do with three liquids, hexane, benzene, and carbon disulphide. They were chosen as supposedly non-associated liquids, though I have shown that in the dry state they are associated to such an extent that the average size of the molecules is at least twice the size of the single molecule. The liquids were dried only as far as concentrated sulphuric acid could do so, *i.e.*, there would still be a large number of water

molecules diffused through the molecules of the liquid. The boiling point of the benzene was 79·6°. Tubes of 1 cm. diameter were prepared with two platinum plates, about 7 cm. long, fixed facing each other at the lower end of the tube. A thermometer was placed between them. Benzene was introduced just to cover the plates (Fig. 3). By connecting the platinum plates with a 400-volt battery for some hours, the boiling point of the benzene was raised to 91°. A precisely similar tube containing the same benzene and similar electrodes, but without the applied voltage, was placed in the same bath; the benzene boiled at 79·6°. This effect was not destroyed when the apparatus stood for a few days with the plates disconnected from the battery; the boiling point was 88° and the boiling was steady, not violent. While the boiling was proceeding, the voltage was again applied and in two minutes the evolution of bubbles stopped. Measurements of the surface tension of the liquid indicated a molecular weight of between two and three times that corresponding to the formula C_6H_6.

This experiment, which is confirmed by similar behaviour with hexane and carbon disulphide, may be explained by supposing that the ions were removed by the electric field and therefore the water present was incapable of collecting into drops.

I thought that the effect might possibly be due to the elimination of water by electrolysis and the consequential drying of the liquid; not a trace of gas, however, could be collected over the mercury in the trough. Moreover, if the plates were connected together and allowed to stand, the surface tension indicated a normal molecular weight, and the normal boiling point was restored.

If further work on these lines should confirm the result of these preliminary experiments, we shall have, for the first time, an explanation of the rôle played by water in changes of molecular association in liquids.

I wish, in conclusion, to express my thanks to my wife and to Miss Carlton for their help in the experiments which I have described.

OBITUARY NOTICES.

LUCY HIGGINBOTHAM.

BORN, NOVEMBER 6TH, 1896; DIED, NOVEMBER 22ND, 1927.

LUCY HIGGINBOTHAM was educated at Penrhos College, Rhos-on-Sea, and the Manchester High School for Girls. She entered Manchester University in the autumn of 1915, and took the Honours course in chemistry, graduating with First Class Honours in 1919 and gaining the Leblanc Medal for the Chemistry of Colouring Matters. The following year was spent in work on derivatives of coumarone which earned her the degree of M.Sc., and was published in the *Transactions* jointly with Dr. Henry Stephen (J., 1920, **117**, 1534). For the next two years she acted as research assistant to Professor Arthur Lapworth, F.R.S., and contributed with him to the *Transactions* of the Society five papers dealing with the reactions of ethyl ethylidenemalonate and related substances (J., 1922, **121**, 49, 2823; 1923, **123**, 1325, 1618; 1924, **125**, 2339). In September 1922 she joined the staff of the British Cotton Industry Research Association, and was elected to the Fellowship of the Society in December of the same year. For the remainder of her active career she was engaged in researches on the minor constituents of cotton, in particular the complex mixture of substances present in cotton wax, and their behaviour during the processes concerned in the bleaching and finishing of cotton, the results being contained in a series of papers in the *Textile Institute Journal* (1924, **15**, T75, T120, T337; 1926, **17**, T233; 1927, **18**, T283), and in the *Memoirs* of the Shirley Institute. Early in 1926 illness necessitated a rest of several months. She returned to work again, but, after a relapse, went to Berne on the advice of her medical adviser for an operation, and died there on November 22nd, 1927. As a research worker she possessed unusual energy and a pronounced *flair* for the rapid exploration of a field of inquiry; outside her work, she was keenly interested in athletics, particularly tennis, golf, and motor cycling. She had many of the best characteristics of her native county, and her frank outspoken genial personality endeared her to her colleagues at the University and the Shirley Institute.

R. G. FARGHER.

EDWIN ROY WATSON.

BORN, JULY 20TH, 1880: DIED, NOVEMBER 10TH, 1926.

EDWIN ROY WATSON, the second son of William Watson, was born on July 20th, 1880, and received his early education at the Nottingham High School (1891—1899), where his career throughout was marked by high distinction. Although in 1897 he obtained an open science scholarship tenable at Emmanuel College, Oxford, this was not utilised, and he first graduated as an external science student at the London University in 1900. As the result of a second scholarship award, he became a student at Jesus College, Cambridge, in 1899, subsequently taking a First Class in Part I of the Natural Science Tripos (1901), and a second class in Part II (1903). From 1902—1904 he was mainly engaged in post-graduate research at Cambridge, under the direction of Dr. S. Ruhemann, although during this period he also took part in a temperature survey of Loch Ness, then in progress under Sir John Murray's direction. In 1904 he was appointed Professor of Chemistry to the Sidpur Engineering College, Bengal, where he remained for two years, then proceeding to Dacca College in a similar capacity. In 1921 he became Principal of the Government Technological Institute at Cawnpore, and with this institution he was still connected at the time of his death.

Watson was characterised throughout his career by thoroughness and tenacity of purpose. Being an excellent chemist and an able lecturer, and possessing an almost untiring energy, his influence with his students was most marked, and as a teacher at Dacca he will long be held in affectionate remembrance.

At the outset of his work at Dacca the College possessed no laboratory worthy of the name, and although on its removal to Ramna, and under his guidance, this defect was remedied, for a long period many conveniences were lacking and the conditions essential for good work were far from ideal. Even in these circumstances, however, he was able to prepare the students for their degree examination in science. But Watson was not satisfied with the mere routine teaching of science; he was at heart an investigator, and by untiring effort he was gradually successful in creating an atmosphere of research amongst his more advanced students. This was no mean task to undertake amidst the enervating influence of the climate and the many distractions of Indian life, but with this object he was at work both early and late, without regard to his personal convenience. The zeal for work of this character which he created is still in evidence at Dacca, and there can be no doubt that his influence has played no small part in the development of the

research spirit which is now becoming prominent throughout India.

As a true teacher Watson sought to know his students and to learn their difficulties. He freely mixed with them, gained their confidence by means of his characteristically simple manner, and indeed encouraged those engaged upon research to visit at his home.

When appointed at the newly established Institute at Cawnpore, Watson at once devoted himself to its thorough organisation. This establishment, which was founded as an aid to the industries of India, not only undertakes the investigation of native products, but acts as a teaching centre for those post-graduate students who desire to take up technology as a career. Though here again Watson has left an excellent record of work, and his zeal for the welfare of the Institute was always clearly evident, it became apparent to his intimate friends that he was not so happy at Cawnpore as he had been at Dacca, and that he much regretted the cessation of his former opportunities for work in the domain of pure science.

Watson was keenly interested in the formation of the Indian Chemical Society, of which he became a Vice-President, and to him, without doubt, its inception was largely due. At the meeting of the Eleventh Indian Science Congress he was appointed President of its Chemical Section, and in his address pleaded for the better organisation of research work, the freer intercourse between manufacturer and pure chemist, and a more general discussion of chemical problems the solution of which was urgently required.

Watson's work at Cambridge, which was embodied in three papers, two carried out with Dr. S. Ruhemann, and the third independently, was concerned with the chemistry of the β-diketones (J., 1904, **85**, 456, 1170, 1319). His first investigation carried out in India (J., 1906, **89**, 578) was of a very different type and consisted of a study of the decomposition products of silver peroxynitrate under the influence of boiling water.

In 1912 Watson's attention was directed to the *Cydnus Indicus*, an insect which at Dacca is attracted by artificial light, and is notorious for its strong and unpleasant odour. This arises from the excretion by the insect of a volatile oily fluid, and Watson ascertained that it was due to the presence therein of *cyclo*heptanecarboxylic acid (of which 1½% was present in the insect), though a trace of a second substance ($C_{11}H_{20}O_2$?) could also be isolated. The odour is so intense that the oil excreted by one insect, which averages 0·000005 g., is sufficient to render its presence apparent.

With the exception of these earlier researches Watson's scientific work deals almost entirely with the vexed question of the origin of

colour in dyes, and the effect of structure on colour intensity, problems which fascinated him throughout his career. His many contributions on this subject, which are of first class importance, are too well known to require discussion here, and it is certain that his name will long be remembered in this connexion. In 1913, while in England on leave, he occupied himself at the Clothworkers' Research Laboratory, University of Leeds, with an investigation of flavonol colouring matters, which secured for him the Doctorate of Science in the University of London in 1914.

During 1916 to 1918, Watson was again on leave in England, and throughout this period he was engaged on investigations mainly of a technical character on behalf of the British Dyestuffs Ltd. at the University of Leeds. Whilst there, he gave a course of lectures on "Colour and Constitution" to works chemists, and these he employed later as the basis of his well-known monograph having that title (Longmans Green & Co., 1918). This volume, in which the various aspects of the subject are critically considered, indicates the author's complete mastery of his subject.

His work at Leeds, concerned as it was with processes of dye manufacture, was mainly of a confidential character, although later on he was enabled to communicate to the Society (J., 1921, **119**, 1211) the continuation of his earlier investigation on the preparation of dyes from phenanthrene (*J. Soc. Chem. Ind.*, 1915, **34**, 1136). Though his attempts to prepare phenanthrene analogues of the anthraquinone mordant and vat dyestuffs were unsuccessful, certain new azine derivatives of this hydrocarbon were obtained. His final papers (Mazumber and Watson, J., 1920, **117**, 830; Watson and Dutt, J., 1922, **121**, 1939, 2414), which were concerned with the "Constitution of Yellow Sulphide Dyes," and "Attempts to prepare Red Sulphide Dyes," give evidence of patient work and are of much interest.

Whilst Principal of the Cawnpore Institute, Watson was responsible for some twenty communications, of a technical character, to the *Journal of the Indian Chemical Society*, which are connected with the utilisation of Indian natural products. Amongst these may be cited a description of a satisfactory process for the refinement of the "Neem" oil derived from *Melia azadirachta*, which, though available in considerable amount, possesses an objectionable odour and an intensely bitter taste; methods for the preparation of T.N.T. from Assam and Burma petroleums; and trials indicating that Himalayan oak hark (*Quercus incana*) can be employed commercially as a source of tannin extract.

Watson was an ideal manipulator: he was precise and tidy at his work, and although somewhat deliberate in his methods was

by no means slow in attaining his results. Of a modest and retiring disposition, possessing a somewhat nervous manner, and being absorbed in his work, he appeared at first sight somewhat difficul of approach, but this was in reality not the case, and to those wh sought to know him he exhibited a delightful personality. Straight forward, and out-spoken when necessity arose, his sense of justic was extremely keen, and he was a rigid disciplinarian. In th circumstances of his life abroad, his intercourse with scientifi equals was of infrequent occurrence, a disadvantage which he keenl felt, and although this at one time almost decided him to seek a appointment at home, on consideration it seemed unwise to abando the advantages to which his long stay in India would shortly entitl him. In view of the parlous condition of chemical research i India when he arrived there in 1904, it is remarkable that he wa able to accomplish what he did, no mean achievement indeed ha he possessed the advantages of a similar position at an Englis University.

Watson's life in India was simple in the extreme, his main recre ation being painting in water colours. Of this he was an excellen exponent, and he exhibited, with success, at Simla, Nana Tal, an other fine-art exhibitions.

During the last two years of his stay at Cawnpore, Watson becam subject to fits of great depression, and eventually, as the result of a nervous breakdown, he obtained leave of absence from India i April 1926. Failing to obtain relief by a visit to Switzerland, he returned to London, where his sudden death occurred. He ha hoped to investigate further laccaic acid, the colouring matter of la dye, and for this purpose had arranged for laboratory accommodatio at the Imperial College of Science. A letter on this subject to the author of this notice was one of the last, if not the last, he wrote.

Watson married Lily Mary Hurlston of Leamington Spa i October 1908, and had two children who died in infancy.

A. G. Perkin.

HORACE BROWN.

1848—1925.

Iorace Brown was born at Burton-on-Trent, July 20th, 1848. le died February 6th, 1925. He was elected a Fellow of the 'hemical Society in 1871. He first served on the Council 1883—7; hen as Vice-President 1894—7, 1904—7, 1913; as Treasurer 903—4; as Foreign Secretary 1907—13. For reasons of health, e was unable to accept the Presidency. He was awarded the ongstaff Medal in 1894.

I have told the history of the Brown family and not a little of Iorace's in my Adrian Brown Memorial Lecture to the Institute of 'rewing (1921). He himself gave to this Institute a very full ccount of his career, in his " Reminiscences of Fifty Years Experiences of the Application of Scientific Practice to Brewing Practice .918)."

He attended the local Grammar School from the age of nine years awards, exchanging this for Atherstone Grammar School during 864. He left school when 15½ years of age. He was well drilled Latin and Mathematics and even learnt some Greek; years terwards he polished up his Latin for the London Matriculation, ith the result that, in his declining days, he again read Virgil with terest.

Through his classical training at school—and home practice I elieve—he learnt to have regard for words and to express himself early, with simple elegance: it was never in his nature to be either ireless or florid. His real education was out of school. The father, ng manager of the Burton Bank, was a man of unusual ability and naturalist (coleopterist) of repute; he was also both botanist and ologist. He had a large circle of scientific friends, some of whom casionally came to stay at the bank. The boy was thus early ought into contact with the scientific mind and grew up in an dered, intellectual atmosphere. In their walks abroad with the ther, the boys (Horace and Adrian) became trained field workers id close observers. Later on, Adrian developed more as botanist d fisherman, whilst Horace became more specially interested in ology. An elder sister was a good pianist and Horace had musical oclivities, which she helped him to develop. He was a fair ello player and a great lover of Beethoven but in music was never modernist and so never acquired Wagner.

When about twelve, of his own accord, he began to pay serious tention to astronomy. Next he toyed with electricity. On ming into possession of a microscope, as a gift from his father,

he soon became an ardent systematic student of natural objects, especially of pond life. At fifteen, he was fascinated by Tyndall's " Heat as a Mode of Motion " and also began to take up chemistry experimentally; he seems to have soon found his métier here and to have devoted all his school leisure to the study. In the course of a couple of years, he worked through the qualitative Fresenius in the laboratory he improvised in a storeroom. At this time, he learnt to know Peter Griess, who undoubtedly had great influence in forming the bent of his boyish mind, helping him as he did to make his work systematic.

We met, at the Royal College of Chemistry, in the spring of 1865, just before Hofmann left for Germany. We became friends at once and remained so, without ripple of disturbance, up to his death in 1925. On entry he was far better prepared than are most students at the end of their first year—and through his own efforts. I well remember how we romped through the course. We were in the first bunch of Frankland's students and were used by him as immediate tests of the system which he put forward shortly afterwards in his " Lecture Notes." We became past masters in the art of constructing " imaginary " constitutional formulæ. Consequently, structural chemistry grew into a habit with me and I am satisfied that the opportunity put me years ahead in my outlook; the task did not make the same appeal to Brown: he was never much interested in " futures."

Brown's career at the College was a short one, as at the end of the year, when barely 17½ years old, he accepted an appointment as Junior Brewer in Worthington and Co.'s brewery, next door to his home. We do well, in these pampered days of educational spoon-feeding and examinations, when boys are kept at school up to nineteen years of age and deprived of all opportunity of developing individuality and learning the ways of the world, to reflect on the fact: to realise that the man who ultimately took the Copley Medal had less than six months' systematic academic training in chemistry or, for that matter, in any other branch of science. Fortunately he was not taught but learnt nearly everything and by his own unaided efforts, the " urge " to do something being upon him. Probably, his success was not so much due to great intellectual power as to his unwearied, determined habits of study, to his breadth of outlook and the sanity of his judgment. In the widest sense he was a born naturalist. Finally, he became the scientific amateur of high distinction—if not the only representative Chemistry has had in this remarkable English species, certainly to be placed in the front rank.

As Junior Brewer, his working time was twelve hours a day

There was no regular Saturday half-holiday and he was expected to watch things on Sunday. None the less, he continued his private scientific studies—first in an old glass-house, in his father's garden, adjoining the brewery; then in a small laboratory which his father built specially for him. He worked under Griess's direction and occupied himself in preparing and studying the base from nitrobenzonitrile. The only way in which he was *allowed* to use his scientific knowledge in the brewery was in determining original gravities of beers. At the close of the brewing season, in May 1868, he spent a few weeks in Frankland's laboratory, studying the combustion method of water analysis which Frankland and I had just introduced. On his return, he installed the necessary apparatus in a small room which received the courtesy title *Laboratory*. He then set to work to analyse the well waters used in his own and other breweries and also the Trent and the parish pumps. The verdict of "sewage" which he returned in many cases led to the cleaning up of the water supply of the district. During several years he both thought and talked "sewage mostly." Later on (about 1883), in connexion with this work, he was led for a time to take up geology seriously and eventually contributed a valuable memoir on the Permian rocks of the Leicestershire Coal Field to the Geological Society (1889).

Three or four years after entry into Worthington's, when he had mastered brewing practice, mindful of his youthful experience, he turned to the microscope. His immediate object was to discover the cause of "caskiness" in beer. He ultimately traced the trouble to the growth of the blue mould, *Penicillium glaucum*. He was thus led to study yeasts, more particularly as at this time (1870) he became acquainted with Pasteur's *Études sur le Vin*; he at once saw the application to beer of the principles laid down by Pasteur for wine. He had already developed the method of ascertaining the "fate" of beers in advance by "forcing," prior to the appearance (1876) of Pasteur's second great work *Études sur la Bière*, which was to revolutionise brewing practice.

Such was the progress he made, that in 1873, at the age of 25, he became Manager of the whole of the manufacturing department of Worthington's Brewery, a post which he occupied until 1889, when he became a Managing Director, on incorporation of the firm as a limited liability company. He retired in 1893 and left Burton for London, where he engaged in scientific work up to the year 1917. He married in 1874.

A few months after Brown became chemist to Worthington's, his former teacher at the Royal College of Chemistry, Cornelius O'Sullivan, who had accompanied Hofmann to Berlin to act as his

lecture assistant, was appointed chemist to Bass & Co. As is well known, one of his first acts was to study the hydrolysis of starch under the influence of malt diastase. He rediscovered maltose, which chemists had forgotten. He also showed that starch was resolved into maltose and a dextrin, in proportions which varied according as the diastase had been more or less heated. His results were a great revelation to the brewing industry. A few years after Brown became Manager, he secured an assistant, John Heron, with whom, about 1877, he began a revision of O'Sullivan's work. The inquiry was continued during many years (until 1899), in conjunction with Morris, Millar and others. The results, although not identical with O'Sullivan's, were of the same order. Various other workers have met with no better fate—starch is still an unsolved riddle. To-day, we know little more in principle than O'Sullivan taught us—though there is reason to think that we may be near to a correct interpretation. Probably, several enzymes are concerned in the malting process; we are assured also that "starch" is a complex material. That so much energy should have been spent and wasted in solving the starch problem is little short of deplorable —and but proof that we are far from having systematised our methods of attack. Brown probably ought to have known better than to undertake such a task: had he known more chemistry, he would scarcely have attempted it, at least until he had laid simpler and solid foundations.

About 1887, with an effort, he cut himself adrift from geological work, in order to take up the study of the malting process, then in an empirical state. Discovering how ill-equipped he was for the inquiry, he first set to work to give himself a solid grounding in physiological botany generally. This he obtained, he tells us, in a few years time, by hard work during his leisure hours. The final result was the memoir presented to this Society in 1890, by Morris and himself, *Researches on the Germination of some of the Gramineæ.* This, from the beginning, took rank as a classic and his work placed the malting industry upon a sound scientific basis.

His genius was even more fully displayed in the inquiry he then undertook, which he brought under the notice of the Society (in conjunction with Morris) in 1893, in the memoir *A Contribution to the Chemistry and Physiology of Foliage Leaves.* This again took rank as a classic. One of the most striking conclusions arrived at was, that the first visible product of assimilation in plants, under the influence of chlorophyll, was not starch but cane-sugar.

After his retirement from Burton, he continued the study of the assimilation process, particularly the absorption of atmospheric carbon dioxide by green leaves. Much of the work was done at

Kew, in the Jodrell laboratory, in conjunction with F. Escombe. They were able to show, for the first time, how it was possible to account for the sufficiently rapid ingress of carbon dioxide from the atmosphere to supply the leaf on the assumption that interchange took place only through the stomatal openings. Here again he laid solid foundations and captured the sympathy of all vegetable physiologists. The work was followed by a series of studies of the fundamental phenomena of gaseous and liquid diffusion.

These brief references may suffice to indicate the character and range of his activity but are no measure of its intensity. A full discussion of his work will be given in my Horace Brown Lecture to the Institute of Brewing.

As a man, he attracted all with whom he was in contact by his appearance and engaging courtesy of manner. In person strikingly handsome, in his later years especially, his face stamped with intellectuality, gifted with a most alluring persuasive voice and mode of address, in outlook a man of high refinement but great simplicity, appreciative of all forms of culture, he yet displayed no special leanings towards artistry other than his love of music: his tendency, indeed, was rather matter of fact. Without angles, he was never assertive, although very firm in his opinions. Although an engaging conversationalist, he was always peculiarly reticent in speaking of himself and his own doings, even secretive. Almost entirely self-trained in science, he had an extraordinary faculty for getting up a subject and a high sense of values. Whatever he did, he did thoroughly. Although he had no great depth of knowledge, he had great feeling, especially for vegetable physiology. Probably this is why—apart from his work on starch—he was so successful in selecting and solving fundamental problems.

In 1916, at the meeting of the Institute of Brewing to which he communicated his Reminiscences, in proposing the vote of thanks, I spoke of him as "An original inquirer, to the manner born: the methods he used," I said, "were the reflexion of his own personality, of exceptional finish, penetrant and always philosophical. . . . He had always shown an instinctive sympathy with vital phenomena, a penetrative appreciation of the physiological significance of chemical and physical phenomena such as is very rarely met with in the chemist."

In fact, he had the universal mind and could not be better described than he is, by implication, in the following passage, in a recent work on literary criticism, by Mr. Herbert Read:—

"It has been a common saying, since Pope first said it, that a little knowledge is a dangerous thing but far more dangerous is the knowledge which, though not little, is limited. It is idle to

think that any good can come of a *specialisation that is not* linke to some wider ethos or that is not subordinate to general wisdom an this applies not only to the scientist whom we regard, rather rashl as the only specialist but equally to the critic and the poet. may be said, that the rare occurrence of a universal mind, as i Aristotle, Leibniz or Goethe, is the definite result of a *lusus natur* of chance, in fact . . . universality is a quality possessed by a the rarer spirits of any age. . . . It does not mean the possessio *of all knowledge* or even *necessarily of any knowledge* at all. does imply a capacity to receive all knowledge and events wit equanimity and unprejudiced percipience and to build up a positi attitude on this clear and secure perceptual basis."

HENRY E. ARMSTRONG.

SIR JAMES DEWAR.

1842—1923.

JAMES DEWAR was born 20th September, 1842. He died 27t March, 1923. Elected a Fellow of the Chemical Society, Decembe 1st, 1870, he first served upon the Council 1874—77. He wa *Vice-President, 1880—83, 1886—88, 1896—97, 1899—1921.* H was President, 1897—99.

The writer has attempted to picture the man—an impossibl task—in a Friday evening Lecture to the Members of the Roya Institution, delivered on 18th January, 1924.* He had previousl summarised his work at low temperatures and his work generally as Fullerian Professor, up to 1917, in two essays, one on *The Charcoa Vacuum Septenate* (1909), the other on *The High Vacuum Septenat* (1917), both published in the Proceedings of the Royal Institution During his lifetime, the spectroscopic work he did with his colleague Prof. Liveing, was published in a volume of their Collected Paper (1915). The papers describing his chemical and physical worl have been collected and published in two large volumes, like that o spectroscopy, printed at the Cambridge University Press (1927).

Dewar was educated at the Dollar Academy (1855—58), wher he was distinguished in Mathematics. He entered as a first yea Arts Student at Edinburgh University in 1859 and was on th register during the two following years. He first came under th influence of David Forbes, the distinguished physicist, also a geologis of repute. When Forbes left Edinburgh to become Principal o St. Andrews, he gave Dewar the chemical case he carried with hin

* Published separately, in advance of the Proceedings of the Institutio for the year, by Ernest Benn, Ltd., London.

in his European travels. When he left Edinburgh for Cambridge, Dewar gave it to his nephew, Dr. T. W. Dewar, who has presented it (1923) to the Royal Society of Edinburgh. Dewar was a distinguished student in Tait's class.

When Lyon Playfair, the Professor of Chemistry, was able to take on an assistant, he engaged Dewar. On Playfair's retirement, in 1868, Dewar became assistant to Crum Brown; he taught the Medical laboratory class. In 1869, he was appointed Lecturer and later Professor of Chemistry in the Royal Veterinary College. In 1873, he also became assistant chemist to the Highland and Agricultural Society of Scotland. In 1875, he was appointed Jacksonian Professor in Cambridge. In 1877, he became Fullerian Professor of Chemistry in the Royal Institution. He held both chairs up to his death.

He began to publish in 1867. In Edinburgh, his work was mainly in organic chemistry. In Cambridge, he devoted himself particularly to spectroscopic inquiry but also did fine chemical work. In London, high temperature and spectroscopic studies first engaged his attention. From 1884 onwards, be devoted himself to the development of methods of reducing the difficultly coercible gases, nitrogen, oxygen and hydrogen to the liquid and solid states and to the study of low temperature phenomena in general. He all but succeeded in liquefying helium but was beaten in the race by the superior resources of the Onnes laboratory. In his last years, he found solace in the soap film. Characteristic of all his work was the elegance and simplicity of his methods. More particularly by the introduction of the vacuum flask, coated internally with silver to reduce radiation losses (*the Dewar Flask*), he made possible the use of liquid air and liquefied gases generally as refrigerating agents. To him, in fact, is due the introduction of liquefied gases as weapons of research at very low temperatures. Later, by his discovery of the marvellous absorbing power of properly prepared charcoal at low temperatures, he greatly improved the methods of producing very low vacua. The immensity of the service he thus rendered, both to philosophical inquiry and to industrial progress, although admitted, is not sufficiently recognised—especially in Germany, where his inventions were quietly appropriated with little if any acknowledgment.

The student of the Dewar Papers has a rich store before him. He will find something of interest and of value upon almost every page, if not in almost every paragraph, if he have imagination and reflect upon the lessons that may be read upon and between the lines. We are carried back to the days when the flood-tide of organic chemistry was but beginning to rise: the curtain goes up shortly

after Kekulé had propounded his views upon the constitution of benzene (1865), with Crum Brown and Kekulé as prompters. Thus, in the opening lines of the first chapter of the first book, attention is directed to the importance of *oxidation*, as a means of determining structure, in the following terms :—

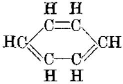
"The syntheses and oxidation analyses of organic compounds have so confirmed each other in many *cases, that chemists are enabled to judge of the structure of a compound from the oxidation* products. Many chemists have used the oxidation method in special cases, the bodies operated upon belonging principally to the fatty series; but until Fittig and Beilstein published their memoirs on the aromatic compounds, it was never applied to the systematic study of a hydrocarbon and its derivatives. But although the syntheses and oxidation analyses of the derivatives of benzol confirmed each other, still the structure of the original nucleus (benzol) remained unexplained. Kekulé's original and elegant speculations on the structure of benzol and its derivatives induced me to try the *effect of oxidising agents on benzol, with the view of eliciting* whether the carbon atoms would separate in the way theory pointed out. The carbon atoms in benzol may be supposed to be arranged in a closed chain, where the carbon affinities are bound two and one alternately. Now, if we examine the formula graphically, it is evident there are three symmetrical groupings, C_2H_2 (acetylene), in benzol. We would, therefore, expect the carbons to separate in twos and produce the corresponding oxidised product, $C_2H_2O_4$, oxalic acid."

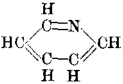
Failing to oxidise benzene with permanganate, Dewar took phenol. He obtained oxalic acid and thought that possibly either *fumaric* or *mellitic acid* (!) was formed. He ends with the remark—"The application of permanganate of potash as an oxidising agent in organic chemistry promises interesting results." The special feature of interest in the paper, however, is the description that is given of "a simple mechanical arrangement adapted to illustrate structure in the non-saturated hydrocarbons. This little device is the mechanical representative of Dr. C. Brown's well-known graphic notation." An elaborate diagram is given showing 7 different ways of associating 6 carbon atoms, among them being the well-known arrangement often referred to as Dewar's benzene formula, although he in no way specially calls attention to it. In the closing words: "Naphthalene and many other hydrocarbons give elegant symmetrical diagrams when represented as a closed circuit," we have a clear forecast of the utility of Kekulé's conception.

In the summer of the year (1867) in which he published this, *his* first paper, Dewar spent some time in Kekulé's laboratory at

Ghent. Under Kekulé's direction, he there applied permanganate to the oxidation of coal tar bases, particularly picoline. The work was not completed and published until 1870. The paper contains the following noteworthy passage.

"Pyridine may be written graphically as benzol in which nitrogen functions in place of the triatomic residue CH‴ and thus may be represented as a closed chain.





And, considering the stability and mode of formation of these bases, it is not at all improbable that they may be produced by the simultaneous action of acetylene and its derivatives on hydrocyanic acid; thus as three molecules of acetylene condense and form benzol, so may two molecules of acetylene and one of hydrocyanic acid condense and produce pyridine."

Someone has yet to discover means of effecting both these syntheses economically.

In Ghent, Dewar became very intimate with Kekulé's assistant Körner, to whom far more than to Kekulé we owe the early development of the position chemistry of benzene—to which Kekulé himself attached no particular importance, in no way foreseeing its great applications. The two men, both in the flush of youth, we know, were a wild pair—thoroughly congenial spirits. The association, short as it was, with such a master-worker was of the greatest value to Dewar; he preserved his affection for Körner to the last. We often talked of him together. Whilst Kekulé was the man of affairs, as one so strikingly handsome and eloquent was bound to be, a philosopher and dreamer, Körner was reserved and a laboratory worker but of incomparable skill. He gloried in preparing fine crystals. He it was who first saw the practical potentialities of the Kekulé hypothesis. Using the mere sketch Kekulé, as architect, had provided, he quietly put together a finished building of considerable size and suddenly unveiled this, in all its perfection, to our astonished gaze, choosing the language of his adopted country, Italy, for his description of the work. When Henry Watts asked me to abstract the memoir for him, I did not know a word of Italian. On turning over the pages, I was so attracted that, with dictionary and grammar bought for the purpose, I soon puzzled out the wonderful story. Such abstracting was indeed joy—I have never engaged in a more fascinating exercise. Why do not more young chemists learn to take an interest in languages in this way? Is reading a

lost art—is Liebig's well-known advice to Kekulé altogether forgotten? Dewar was privy to Körner's work and ever worshipped his manipulative skill. The experience made him an organic chemist—although he soon ceased from regular active participation in organic inquiry. Seeing an army of locusts coming down upon the field, ever impatient of pot-boiling and uniformity, he gradually extended his operations into then almost unpeopled regions. He had most wonderful fingers and a sufficiently mathematical mind, full of physical lore, to find that ordinary laboratory work did not afford the variety and kind of occupation his soul desired. The vast potentialities of structural chemistry were then scarcely apparent. He had the foresight, which all but the few lack, to realise that he must train himself to work in any field.

In 1868, Dewar exhibited at the B.A. meeting "a model devised by Professor Kekulé to illustrate the structure of organic compounds. He explained the peculiarity of the model consisted in carbon, with its four atomicities, being represented by a small sphere, with four equal wire arms joining the centre of the sphere with the angle of an imaginary equilateral tetrahedron." *

We have here an independent record of Kekulé's unwitting anticipation of his pupil van 't Hoff's happy use of the tetrahedron as the model of the carbon atom—a conception now established in the realm of fact by Sir William Bragg's inspired study of the diamond.

Latent in Dewar was the spirit of physical inquiry. Not only had he wonderful fingers, he was an insatiate experimenter, one who loved just to try things, to see what would happen; moreover, he was in contact with the physicist Tait. Chemico-physical inquiry gave him opportunities which organic chemistry did not seem to offer. So it comes that, among his early contributions, some are semi-physical. In his lectures at the Royal Institution, he never failed to grip his audience, not by his eloquence nor by the clearness of his expositions—actually he was difficult to follow—but by the extraordinary display he made of experimental illustrations which fascinated by their elegance and originality. Faraday took pains but he handled simpler themes. Dewar took more than pains. The stock illustrations made no appeal to him but he developed lecture-demonstration to a fine art. In the course of sixty years I have listened to all the great lecturers on Friday evenings—others may have told their story more clearly, more convincingly; no one has ever approached him in the calculated perfection of his illustrations. He regarded the lecture as an artistic performance to be staged with absolute forethought and utmost care, provided with original scenery and all necessary appointments, without coun

* Compare Japp: Kekulé Memorial Lecture.

of cost. He had the same ambition in the R.I. lectures that his friend Irving, the great actor, had on the Lyceum stage.

The accounts on record give but the faintest idea of the performances we witnessed. Only those who have seen the two men on their respective stages have any clear idea of the way in which their actions were adjusted to and supported by their surroundings. Neither was the mere professor: both men were artists through and through.

Dewar's artistry is already apparent in the fifth of his recorded compositions—that on the motion of a palladium plate during the formation of Graham's hydrogenium. Graham was then Master of the Mint—my fellow-student, Roberts Austen, was the assistant who carried out the hydrogenium experiments for him. Dewar, through Playfair, had known Graham in Glasgow and, of course, was attracted by his work. "During the course of an experimental exhibition of Graham's discovery, I noted several phenomena associated with the occlusion of hydrogen by palladium, when it is made the negative electrode during the electrolysis of water; and as they illustrate, in a new form, the results already arrived at by the Master of the Mint, with his permission, I am induced to bring them before the Society," are the words with which he explains the origin of his attention to the subject. The peculiar behaviour of palladium towards hydrogen is illustrated in the most perfect manner in the memoir.

From palladium we pass to chlorosulphonic acid (B.A. 1869, with Cranston). To me, this essay is specially interesting, as at the same time I was doing practically the same work at Leipzig, using sulphuric anhydride alone, whilst Dewar and Cranston used it in conjunction with hydrogen chloride. The object they had in view was to study the action of the sulphonic chloride, SO_3HCl, upon phenol, as a sulphonating agent. Finding that they had been anticipated by Engelhardt, they attempted to prepare Kolbe's $CCl_3{\cdot}SO_3H$ by sulphonating chloroform and instead obtained carbonyl chloride, hydrogen chloride and sulphur dioxide, the chloride acting as if it were sulphuric anhydride, as it often does.

They also found that when heated with carbon disulphide, it gave rise to carbonyl sulphide and sulphur dioxide. Commencing with the anhydride, SO_3, I had attempted to prepare sulphonic chlorides of the chlorinated methyls but instead obtained carbonyl chloride and $S_2O_5Cl_2$ from carbon tetrachloride and the same products as Dewar and Cranston from chloroform. I also prepared carbonyl sulphide from carbon disulphide and sulphuric anhydride. Dewar and Cranston remark "probably the reaction (with SO_3HCl) would succeed better by the action of SO_3."

At that time, not a few of us were all working in one direction Engelhardt, as well as Dewar and Cranston, under the spell o Kekulé's hypothesis, were studying the formation of isomeri derivatives of benzene, I also had begun (1868), at Kolbe's sugges tion, to work on phenolsulphonic acids. Desiring to have anothe string to my bow, after reading Robert Williamson's account o chlorosulphonic acid, being familiar with sulphonic anhydride, i occurred to me to attempt to prepare ethereal derivatives of th chloride from the chlorinated hydrocarbons. I began with ethy chloride and was studying the compound $SO_3ClC_2H_5$ when a forme student of Kolbe's, in the late summer of 1868, the Russian vo Purgold, called on Kolbe, on his way home from Paris, with a pape in his pocket just published in the *Comptes rendus* on the sam subject. So I turned to chloroform, carbon tetrachloride anc disulphide.

An interesting note on the atomic volume of solid substance (1870) deserves notice here. It merely has to do with the alter ation in atomic volume, supposedly of the oxygen, in various oxyge compounds. This is a problem which has often been discussed hitherto with no satisfactory result. We may hope that with th aid of X-ray and crystallographic study, we shall, at no distan date, be ablo to arrive at more definite conclusions. Dewar speciall directs attention to potassium chlorate, bromate and iodate. Th volume of the oxygen in potassium chlorate, supposing the chlorid to retain its volume, is 15, whereas it is only 7 in the bromate and (in the iodate, supposing the iodide to retain its original volume in the iodate. Supposing that oxygen be the dominant element—as it may well be—it is conceivable that bromine in the bromate and iodine in the iodate may be thought of as shrinking to the volume of the chlorine in the chloride—at least, as Barlow and Pope have suggested, that there may be a mutual adjustment, to allow of iso-morphous relationship. In point of fact, whatever we assume, we know nothing of the structure of these substances—whether they be open or closed systems. In the age-long controversy on this subject, no definite evidence either way has been produced.

Dewar worked with his friend Gamgee the physiologist on cystine. He also carried out two physiological inquiries with his great friend McKendrick, another physiologist. The first of these, on the physiological action of light, I know was suggested by Dewar, after McKendrick had expressed the desire to work with him. The experiments were carried out mostly at night, as they involved the practice of vivisection. The inquiry seems to have led to a corre-spondence in the local press, re disappearance of cats from the district. Dewar's interest in the work lay on the physical side, I suspect. I

never discovered that he had any special interest in biological inquiry. The research involved a large amount of very delicate and exact observation and is a brilliant inquiry. The second of their joint investigations was on the physiological action of the chinoline and pyridine bases.

During the period up to 1873, when he left Edinburgh for Cambridge, Dewar was chiefly occupied with organic problems, occasionally interspersed with physical. In these latter, however, he laid the foundations of two of his greatest achievements—the Dewar vacuum vessel and the use of charcoal as an absorbent. In Cambridge, he still dallied with organic chemistry but was soon attracted to spectroscopy. Lockyer had set us by the ears, by his outrageous statements on the subject of elementary decompositions at high temperatures. Dewar could not look on quietly under such circumstances and he entered the field against Lockyer. His immediate colleague was the late Prof. Liveing, a man held in the deepest respect at Cambridge and by all who were privileged to know him. He had been appointed to his Chair in almost primitive times, when chemistry was all but unknown as a subject of systematic study. In character, the two men stood at opposite poles—Dewar being fiery, impetuous, so brimming over with enthusiasm and feeling as to be almost uncontrollable; Liveing, calm, deliberate and highly judicial, never carried away by his feelings. That Liveing learnt to appreciate Dewar's great genius—I will even say to love him—and ever sought to balance his activity was proof of the clearness of his insight and of his magnanimity. He did what few elder men do. Recognising the ability of his young colleague, carried away I am sure by his pertinacious enthusiasm, he practically placed himself at his disposal as his assistant and developed an amazing ability and industry as a spectroscopist. Previously he had published nothing. From 1878 onwards, they produced a stream of memoirs now available in the volume of their collected papers. The work they did together at once took rank as trustworthy, at a time when much loose work was being done. Now that spectroscopy is no longer the empirical subject it was and spectra are subject to rational interpretation, it is to be hoped that the great mass of results they accumulated will prove to be of value.

As years went on, Dewar spent more and more of his time at the laboratory of the Royal Institution. Receiving no proper encouragement at Cambridge, once bitten with a love for low temperatures, he gradually surrounded himself in London with an engineering plant which to-day would rank as ridiculous in its simplicity. With it, however, he effected marvels. He did his work with the aid

of a few chosen skilled assistants. In early days, he was greatly helped by the late Mr. Robert Lennox.

As Jacksonian Professor, he only lectured at Cambridge and had little occasion to deal with students. That he had an eye for special genius is clear, however, first in his selection of Liveing then of Dr. Alexander Scott, to aid him in exact analytical inquiry finally, of the late H. O. Jones, a chemist of unusual ability and great promise, who was associated with him in his work on nickel and iron carbonyls and in the study of carbonic sulphide, CS.

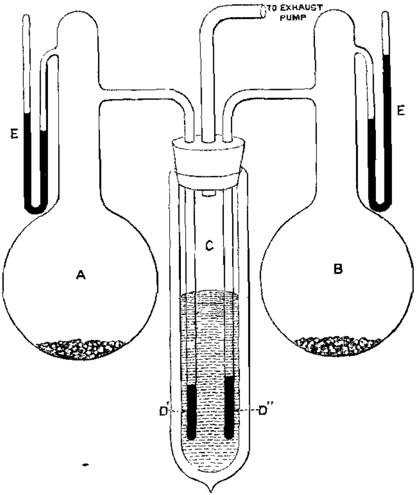
As a good example of the richness of the fare provided in the Collected Papers, the following is taken from his New Researches on Liquid Air :—(I. p. 458):

"*Samples of Air Liquefied in Sealed Flasks.* In a paper 'On the relative behaviour of chemically prepared and of atmospheric nitrogen,' communicated to the Chemical Society in December 1894 the plan of manipulating such samples was described. The arrangement shown in Fig. 4 illustrates how oxygen in A under 0·21 atmosphere pressure and nitrogen in B under 0·79 atmosphere can be compared as to the first appearance of liquefaction in each and finally as to their respective tensions when the temperature is as low as that of solid nitrogen. The flasks A and B have a capacity of more than a litre. Each has a manometer sealed on and in each phosphoric anhydride is inserted to secure dryness. A large vacuum vessel C holds the liquid air, which is gradually lowered in temperature by boiling under exhaustion. The moment liquefaction takes place, the tubes D′, D″ begin to show liquid. These tubes must be drawn fine at the end when accurate observations are being made. In the same manner two oxygen flasks were compared. One was filled with gas made from fused chlorate of potash, contained in a side tube sealed on to the flask. The other was treated in the same way, only the chlorate had a little peroxide of manganese added. The former gave perfectly clear blue liquid oxygen, the latter was turbid from solid chlorine. Two flasks of dry air that had stood over phosphoric anhydride were liquefied side by side, the only difference between the samples being that one was free from carbonic acid. The one gave a liquid that was perfectly clear, the other was turbid from the 0·04 per cent. of carbon dioxide.

The temperature was lowered by exhaustion until samples of liquid air from two flasks placed side by side as in Fig. 4 became solid. The flasks were then sealed off for the purpose of examining the composition of the air that had not been condensed. The one sample contained oxygen, 21·19 per cent. and the other 20·7 per cent. This is an additional proof to the one previously given that

substantially, the oxygen and nitrogen in air liquefy simultaneously, even under gradually diminishing pressure and that in these experiments all the known constituents of air are condensed together. These results finally disprove the view expressed in " A System of Inorganic Chemistry " by Professor Ramsay where he says: " Air has been liquefied by cooling to −192° but as oxygen and nitrogen have not the same boiling point, the less volatile oxygen doubtless liquefies first." My old experiments showed that the

FIG. 4.



substance now known as argon became solid before nitrogen but chemical nitrogen and air nitrogen, with its 0·1 per cent. of argon, behaved in substantially the same way on liquefaction.

Liquid Nitric Oxide.—Great interest attaches to the behaviour of nitric oxide at low temperatures. Professor Olszewski has examined the liquid and describes it as colourless. Samples of nitric oxide have been prepared in different ways. These have been transferred to liquefaction flasks, where they were left in contact

with the anhydrous potash, sulphuric acid alone, a mixture of sulphate of aniline and sulphuric acid or phosphoric acid, for many days before use. Each of the samples, when cooled, gave a nearly white solid, melting into a *blue liquid*. The colour is more marked at the melting point than at the boiling point. Liquid nitric oxide is not magnetic; neither is the solid phosphorescent. Colour in the oxides of nitrogen evidently begins with the second oxide. Solid nitric oxide does not show any chemical action when placed in contact with liquid oxygen provided the tube containing it is completely immersed; but if the tube full of liquid oxygen is lifted into the air, almost instantly a violent explosion takes place."

In fact, the student of the Dewar papers will find them crowded with observations of historic and scientific value in an extraordinarily wide field of chemical and physical inquiry and nothing short of an original conspectus of the properties of matter at the very lowest temperatures, a mine of wealth awaiting exploitation. The lessons to be learnt from them are innumerable. A large part of the matter is put upon record, for the first time, in a way to make it available. In early years at the Royal Institution, Dewar was with difficulty persuaded to put his results upon paper. Much of his work was but briefly referred to in abstract accounts of his Royal Institution lectures. The accounts, therefore, are often not easy to understand and are obviously incomplete. Whatever the interpretation of the records, the two volumes make a most imposing show and probably it is not going too far to say, that no other single worker, except Faraday, has so varied and weighty a record of experimental achievement to his name.

In Sir James Dewar, as in Davy and Faraday, his predecessors at the Royal Institution, the value of genius, unhampered, unrestricted and in the main reliant upon its own efforts, stands displayed before the world in matchless perfection.

HENRY E. ARMSTRONG.

CXXXVI.—*The Oxidation of Nitrophenylcyanoacetates. Part II.*

By Arthur Fairbourne and Harold Richard Fawson.

The oxidation of certain nitrophenylcyanoacetates by chromic anhydride, hydrogen peroxide, and nitric acid has been studied, and the results indicate that the nature of the product depends upon the nitrophenylcyanoacetate rather than upon the agent employed. For example, of the three types of product obtained, *viz.* (*a*) ketonic ester, (*b*) substituted succinic ester, and (*c*) malonamate, ethyl 2 : 4-dinitrophenylcyanoacetate is oxidised to the type (*a*) by chromic anbydride, hydrogen peroxide, or nitric acid; ethyl *p*-nitrophenylcyanoacetate is oxidised to the type (*b*) by chromic anhydride, hydrogen peroxide, or 20% nitric acid; ethyl 2 : 4-dinitrophenylchlorocyanoacetate is converted into the type (*c*) by chromic anhydride or sulphuric acid, nitric acid and hydrogen peroxide having no action under the conditions employed; and ethyl 2 : 4 : 6-trinitrophenylchlorocyauoacetate does not react in any of these ways.

In Part I (J., 1927, 46) the oxidation by chromic anhydride was supposed to proceed through an intermediate hydroxy-ester, $R{\cdot}C(OH)(CN){\cdot}CO_2Et$, but only in the case of a brominated 2 : 4-dinitrophenylcyanoacetate was a compound having the required composition isolated; its formation was regarded as evidence that the bromine atom was in the benzene ring and a hydroxyl group in the side chain. The similar behaviour of the corresponding chloro-compound (*loc. cit.*, p. 50) on oxidation seemed to confirm this view, but the unexpected removal of the halogen by alkali has now indicated that correct formulæ had not been assigned to the two compounds.

When the chlorination product of ethyl 2 : 4-dinitrophenylsodiocyanoacetate reacts in alcoholic solution with the silver derivative of ethyl 2 : 4-dinitrophenylcyanoacetate, some silver chloride is produced together with *ethyl* αβ-*bis*-2 : 4-*dinitrophenyl*-αβ-*dicyanosuccinate*; the yield of the latter, however, never exceeds 50%. This apparent proof of the position of the halogen atom in the chlorination product was therefore rendered indecisive by the

$$\begin{matrix} C_6H_3(NO_2)_2{\cdot}CAg(CN){\cdot}CO_2Et \\ + \\ C_6H_3(NO_2)_2{\cdot}CCl(CN){\cdot}CO_2Et \end{matrix} \longrightarrow \begin{matrix} C_6H_3(NO_2)_2{\cdot}C(CN){\cdot}CO_2Et \\ | \\ C_6H_3(NO_2)_2{\cdot}C(CN){\cdot}CO_2Et \end{matrix}$$

discovery that the same bisdinitrophenyldicyanosuccinate is formed, together with metallic silver, when the silver derivative of ethyl 2 : 4-

dinitrophenylcyanoacetate is boiled alone in alcohol (a synthesis believed to be without precedent; compare, however, Kharasch, *J. Amer. Chem. Soc.*, 1921, **43**, 2239). An attempt to synthesise the same succinate by the action of metallic silver upon the chlorination product alone was unsuccessful.

The position of the halogen atom in the side-chain of the product of the chlorination or bromination of ethyl 2 : 4-dinitrophenylsodiocyanoacetate was definitely established by the preparation of ethyl 2 : 4-dinitrobenzoylformate phenylhydrazone (identical with an authentic specimen; *loc. cit.*, p. 49) from both products.

The alleged hydroxy-esters obtained by the action of chromic anhydride on ethyl 2 : 4-dinitrophenylchlorocyanoacetate and ethyl 2 : 4-dinitrophenylbromocyanoacetate in acetic acid are actually *ethyl dinitrophenylhalogenomalonamates, for they are also formed* by means of sulphuric acid without the use of chromic anhydride, and yield 2 : 4-dinitrophenylhalogenoacetamides on elimination of the carbethoxy-group.

The compounds previously described (*loc. cit.*, pp. 49, 50) as ethyl 2 : 4-dinitrobromophenylcyanoacetate and ethyl 2 : 4-dinitrochlorophenylcyanoacetate are ethyl 2 : 4-dinitrophenylbromocyanoacetate and ethyl 2 : 4-dinitrophenylchlorocyanoacetate, respectively.

EXPERIMENTAL.

Ethyl 2 : 4-*Dinitrophenylchloromalonamate*,
$C_6H_3(NO_2)_2{\cdot}CCl(CO{\cdot}NH_2){\cdot}CO_2Et$.
—(*a*) A mixture of chromic anhydride (0·6 g.) and ethyl 2 : 4-dinitrophenylchlorocyanoacetate (2·5 g.) in 15 c.c. of glacial acetic acid was boiled for $\frac{3}{4}$ hour, some of the solvent was then distilled off, and the residue was poured into water. The product crystallised from alcohol in rhombic plates, m. p. 121°, which gave a purple coloration with alcoholic potash (Found : Cl, 10·9. $C_{11}H_{10}O_7N_3Cl$ requires Cl, 10·7%).

(*b*) A solution of 0·5 g. of ethyl 2 : 4-dinitrophenylchlorocyanoacetate in 2·5 c.c. of concentrated sulphuric acid was kept at 80° for $\frac{1}{2}$ hour and then poured into water. After crystallising from alcohol, the product, alone or when mixed with that described in (*a*), melted at 121°.

2 : 4-*Dinitrophenylchloroacetamide*, $C_6H_3(NO_2)_2{\cdot}CHCl{\cdot}CO{\cdot}NH_2$.—A solution of 1 g. of ethyl 2 : 4-dinitrophenylchlorocyanoacetate in 5 c.c. of concentrated sulphuric acid was heated at 120—130° for $\frac{1}{2}$ hour and then poured into 45 c.c. of water. A brown gum separated, from which crystals were obtained at 0°. These were boiled with charcoal in alcohol and recrystallised, giving white needles, m. p. 134°; on treatment with alcoholic sodium hydroxide, a red-

lish-purple colour developed (Found : Cl, 13·4; N, 16·3. $C_8H_6O_5N_3Cl$ requires Cl, 13·6; N, 16·2%).

Ethyl 2 : 4-Dinitrophenylbromomalonamate,

$$C_6H_3(NO_2)_2\cdot CBr(CO\cdot NH_2)\cdot CO_2Et.$$

—This compound was previously prepared by method (*a*) and erroneously described as ethyl 2 : 4-dinitrobromophenylhydroxycyanoacetate (*loc. cit.*, p. 50). It has now been obtained by method (*b*). The two specimens melted separately or together at 157°.

2 : 4-*Dinitrophenylbromoacetamide* was prepared in an exactly similar manner to the chloroacetamide. It melted at 160°, and gave a deep reddish-purple coloration with alcoholic sodium hydroxide (Found : N, 14·1. $C_8H_6O_5N_3Br$ requires N, 13·8%).

Ethyl αβ-*Bis*-2 : 4-*dinitrophenyl*-αβ-*dicyanosuccinate*.—(*a*) 2·5 G. of the silver derivative of ethyl 2 : 4-dinitrophenylcyanoacetate (*loc. cit.*, p. 48) were boiled with 0·8 g. of iodine in alcohol for ½ hour, silver iodide being formed. The hot filtered solution deposited a solid, which, after being treated with warm ether, crystallised from glacial acetic acid in colourless, hexagonal plates. The substance was not attacked by concentrated nitric acid and gave a red coloration on treatment with alcoholic sodium hydroxide (Found : C, 47·2; H, 3·2; N, 14·9. $C_{22}H_{16}O_{12}N_6$ requires C, 47·5; H, 2·9; N, 15·1%).

(*b*) 2·2 G. of the preceding silver derivative were boiled with an equivalent quantity of ethyl 2 : 4-dinitrophenylchlorocyanoacetate in 20 c.c. of alcohol for 4 hours. The product was isolated from the hot filtered solution as in method (*a*).

(*c*) 1 G. of the silver derivative of ethyl 2 : 4-dinitrophenylcyanoacetate was boiled for 2—3 hours with 10 c.c. of alcohol; metallic silver was then deposited upon the walls of the flask. The ester separated from the hot, filtered solution on cooling, and was purified as before.

The three specimens, alone or mixed, melted at 156°.

Preparation of Ethyl 2 : 4-Dinitrophenylbenzoylformate Phenylhydrazone from Ethyl 2 : 4-Dinitrophenylchlorocyanoacetate and from Ethyl 2 : 4-Dinitrophenylbromocyanoacetate.—Either compound in ethereal solution was slowly added, with thorough mixing, to an excess of ½*N*-sodium hydroxide, and the whole was warmed to 40—50°. The resulting solution was acidified with sulphuric acid and shaken with ether. From the extract, dried over sodium sulphate, an oil was obtained which, upon being boiled in glacial acetic acid with an excess of chromic anhydride for ½ hour and poured into water, yielded a viscous material. This was warmed in dilute acetic acid solution with a few drops of phenylhydrazine for ½ hour; the phenylhydrazone that separated crystallised from glacial acetic acid

in golden-yellow needles which melted, alone or mixed with an authentic specimen (*J.*, 1927, 49), at 170°.

Ethyl 2 : 4 : 6-trinitrophenylchlorocyanoacetate was prepared by treating ethyl 2 : 4 : 6-trinitrophenylcyanoacetate in the theoretical quantity of sodium hydroxide solution with chlorine until the red colour was destroyed. The *ester* separated on warming and shaking, and was obtained in rhombic plates, m. p. 118°, by crystallisation from alcohol (Found : Cl, 9·9. $C_{11}H_7O_8N_4Cl$ requires Cl, 9·9%).

Oxidation with Nitric Acid or Hydrogen Peroxide.—(i) A solution of ethyl *p*-nitrophenylcyanoacetate (2 g.) in glacial acetic acid (10 c.c.) was heated with 2 c.c. of hydrogen peroxide on a water-bath for 20 minutes. On cooling, ethyl αβ-di-*p*-nitrophenyl-αβ-dicyanosuccinate separated; after several crystallisations from glacial acetic acid, it melted, alone or mixed with an authentic specimen (J., 1927, 49), at 209°.

Oxidation with concentrated nitric acid produced *p*-nitrobenzoic acid, but by means of 20% nitric acid at 100° ethyl αβ-di-*p*-nitrophenyl-αβ-dicyanosuccinate was obtained.

(ii) Ethyl 2 : 4-dinitrophenylcyanoacetate (3 g.) was heated with 15 c.c. of concentrated nitric acid on a water-bath for 5—10 minutes until dissolved. Water was added to the mixture, and ethyl 2 : 4-dinitrobenzoylformate then separated as a yellow oil, which solidified after cooling in ice for some time. After crystallising from glacial acetic acid and from alcohol, it melted at 89°, alone or mixed with an authentic specimen (J., 1927, 49).

0·5 G. of the ester, dissolved in a little glacial acetic acid, was heated on a water-bath with an excess of hydrogen peroxide for ½ hour. On cooling, and dilution with water, ethyl 2 : 4-dinitrobenzoylformate separated; it was identified by the mixed melting-point method.

KING'S COLLEGE, LONDON. [*Received, May 26th,* 1927.]

CXXXVII.—*The Mononitrobenzils and the Heteronuclear Dinitrobenzils.*

By FREDERICK DANIEL CHATTAWAY and EDWARD AUTY COULSON.

WHEN benzil is nitrated, three of the six possible heteronuclear dinitrobenzils are formed, 3 : 3′-dinitrobenzil in largest amount and 2 : 3′-dinitrobenzil and 2 : 2′-dinitrobenzil in smaller quantities, the group ·CO·CO· directing the entering nitro-groups into meta- and ortho-positions only (Chattaway and Coulson, J., 1926, 1070). The group ·CH(OH)·, however, which is present in benzoin, i

para-ortho-directing and, although the viscid product of the regulated nitration of benzoin cannot itself be crystallised and separated, the three theoretically possible mononitrobenzils can be isolated from the mixture obtained when it is oxidised by ordinary concentrated nitric acid. 4-Nitrobenzil (I) is thus obtained in considerable amount and 3- and 2-nitrobenzils (II and III) in much smaller quantities.

Each of these three mononitrobenzils can be further nitrated by fuming nitric acid, the second entering nitro-group being directed by the ·CO·CO· group as before mainly into the meta- and to a much smaller extent into the ortho-position in the unsubstituted nucleus. Two of the three heteronuclear dinitrobenzils previously unknown are thus formed as well as the three previously obtained.

In no case has even a slight amount of para-substitution been observed.

It is not, however, necessary to isolate these mononitrobenzils to obtain the new heteronuclear dinitrobenzils, for when a solution of benzoin or acetylbenzoin in excess of fuming nitric acid is kept at the ordinary temperature, dinitration, followed by oxidation, occurs. From the product the two heteronuclear dinitrobenzils previously wanting to complete the series, the 2 : 4′- and the 3 : 4′-dinitrobenzils (V and IV), can be isolated as well as a very small amount of the 4 : 4′-isomeride (VI). The formation of the 4 : 4′-isomeride is possibly due to the orienting influence of the ·CH(OH)· group of the benzoin being slightly effective in the nucleus to which it is only indirectly attached. A small amount of the 2 : 3′-isomeride previously obtained by the nitration of benzil itself is also formed.

The six theoretically possible heteronuclear dinitrobenzils have thus been obtained by the nitration of benzil and of benzoin.

3 : 4′-Dinitrobenzil is dimorphic; the form unstable at the ordinary temperature is of deeper colour and lower melting point than the stable form.

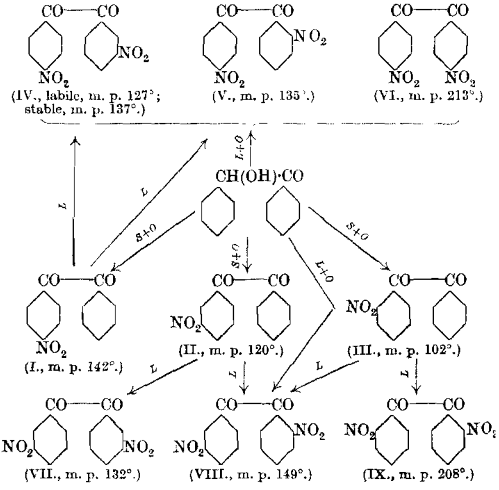
The constitutions of these compounds have been established by oxidising them with chromic acid to the corresponding nitrobenzoic acids. A number of derivatives of each have been prepared serving for their identification.

No dinitrobenzil containing an *o*-nitro-group forms an osazone and both the 2 : 2′- and the 2 : 3′-dinitrobenzil form a monohydrazone only with difficulty.

2 : 2′-Dinitrobenzil also does not form a quinoxaline and is the only one of the mono- and di-nitrobenzils which is not readily oxidised by chromic acid. These peculiarities of behaviour may be ascribed either to the steric or to the polarity effects of the *o*-nitro-groups on the adjacent keto-groups. Both the 4-nitrobenzil and the

2 : 4′-dinitrobenzil yield pairs of apparently structurally isomeric *monohydrazones, but from the other unsymmetrical heteronuclear* dinitro-benzils in each case only a single monohydrazone has been obtained.

The *following scheme shows the mode of formation of the various* mono- and heteronuclear di-nitrobenzils : *S* = regulated nitration in acetic anhydride; *L* = long interaction with anhydrous nitric *acid (d 1·5); O = oxidation with ordinary nitric acid (d 1·4).*



EXPERIMENTAL.

The Regulated Nitration of Benzoin.—By nitration of benzoin (Zinin, *Annalen*, 1864, Suppl. 3, 153; Hausmann, *Ber.*, 1890, **23** 532) or acetylbenzoin (Francis and Keane, J., 1911, **99**, 344) with fuming nitric acid, followed in the latter case by oxidation, it was found impossible to get a good yield of 4-nitrobenzil, the product of nitration being gummy and uncrystallisable. The following method however, gave a good result.

100 G. of benzoin, dissolved in 500 c.c. of acetic anhydride containing 100 g. of concentrated sulphuric acid (whereby the

benzoin was probably first acetylated), were slowly treated at –10° with 55 g. of finely powdered potassium nitrate; the temperature was not allowed to rise above 0°. After remaining for 2 days at the ordinary temperature, the reaction mixture was poured on ice. The cream-coloured, semi-solid mass that separated was removed, drained, and oxidised by boiling with concentrated nitric acid (*d* 1·5; 3 parts by wt.). When no more nitrous fumes were evolved, the solution was poured on ice, and the yellow viscid mass that separated was well washed with boiling water and crystallised twice from acetone and once from alcohol, 50 g. of pure 4-nitrobenzil, m. p. *142°*, being obtained (yield 42%).

The acetone mother-liquors were diluted with alcohol, and a yellow friable mass of crystals, m. p. 103—106°, slowly separated, which contained 3- and 2-nitrobenzils. The former, being less soluble, was obtained by extracting the mixture with insufficient boiling alcohol completely to dissolve it and then crystallising the residue from acetone or alcohol till it melted sharply at 120° (yield, 1 to 2 g. of 3-nitrobenzil). When no more 3-isomeride could be separated, the final residue was crystallised six or seven times from alcohol and yielded 1 g. of pure 2-nitrobenzil, m. p. 102°.

Oxidation of 4-*Nitrobenzil* (I).—A solution of 1 g. of 4-nitrobenzil in acetic acid containing chromic anhydride was boiled for a few minutes, concentrated, and extracted with warm dilute aqueous caustic soda. The filtered extract yielded on acidification 0·94 g. of a mixture of *p*-nitrobenzoic and benzoic acids. The latter was separated by sublimation and had m. p. 121°; the residue on crystallisation from water had m. p. 235° (wt. 0·4 g.). Both were identified by mixed m. p. determinations.

Isomeric Monophenylhydrazones of 4-*Nitrobenzil*.—4-Nitrobenzil (2·45 g.) was warmed with a solution of 1·1 g. of phenylhydrazine in 30 c.c. of alcohol until it dissolved; on cooling, there was obtained a mixture of two substances, which were separated by fractional crystallisation. The less soluble, which was present in greater amount, crystallises in yellow, elongated, rhombic plates, m. p. 200° (Found: N, 12·3. $C_{20}H_{15}O_3N_3$ requires N, 12·2%). The other isomeride crystallises in orange, rhombic plates, m. p. 162° (Found: N, 12·0%). The m. p. of a mixture of the two showed a depression and they appear to be structurally isomeric *monophenylhydrazones* of the formulæ $NO_2{\cdot}C_6H_4{\cdot}C(:N{\cdot}NHPh){\cdot}COPh$ and

$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}C(:N{\cdot}NHPh)Ph.$$

No evidence on which to assign these formulæ more exactly was obtained.

4-*Nitrobenzilosazone* was obtained by boiling the diketone with an excess of phenylhydrazine and phosphoric oxide. It crystallised

from hot acetic acid in very small, orange-coloured needles, m. p. 216° (Found : N, 15·8. $C_{26}H_{21}O_2N_5$ requires N, 16·0%).

2-p-*Nitrophenyl-3-phenylquinoxaline* crystallised from boiling acetic acid, in which it is very soluble, in large, irregular, colourless plates which became opaque and fell to powder when removed from the mother-liquor (probably owing to loss of loosely combined acetic acid), and melted at 161° (Found : N, 13·0. $C_{20}H_{13}O_2N_3$ requires N, 12·8%).

Oxidation and Nitration of 3-*Nitrobenzil* (II).—3-*Nitrobenzil* is readily soluble in boiling alcohol and very readily soluble in boiling acetic acid, acetone, chloroform, and benzene. It crystallises from alcohol in pale yellow, rhombic plates, m. p. 120° (Found : N, 5·4. $C_{14}H_9O_4N$ requires N, 5·5%).

This isomeride on oxidation (for method see p. 1083) gave benzoi and *m*-nitrobenzoic acids, which were separated by sublimation o the former.

The difficulty of preparing 3-nitrobenzil in a perfectly pure stat has hindered the investigation of its derivatives, but it has bee found to be readily nitrated to give a mixture of 3 : 3'- an 3 : 2'-dinitrobenzils. A solution of 1 g. of 3-nitrobenzil in 2 g of fuming nitric acid (*d* 1·5) was boiled a few minutes and then dilute with water. The yellow, viscid, semi-solid product, after beir boiled with water, drained, and dried, soon solidified. It wa crystallised three times from boiling acetone and 0·4 g. of 3 : 3'-dinitr benzil, m. p. 132° (m. p. of mixture with 3 : 3'-dinitrobenzil prepar from benzil not depressed), was obtained. The acetone mothe liquors deposited a mixture of crystals of 3 : 3'- and 3 : 2'-dinitr benzils. By washing these with cold acetone, the former we dissolved away, leaving 0·1 g. of the 3 : 2'-isomeride which, after o crystallisation from acetic acid, had m. p. 149° (m. p. of mixtu with 3 : 2'-dinitrobenzil prepared from benzil not depressed).

Oxidation and Nitration of 2-*Nitrobenzil* (III).—This isomeride similar in appearance to the 3-isomeride, but is rather more solul in all solvents, and the pale yellow rhombic crystals become gre on exposure to light (thus resembling the three heteronucle dinitrobenzils containing one or more *o*-nitro-groups). When pu this substance has m. p. 102° (Found : N, 5·5%). List, who fi prepared it from *o*-nitrodeoxybenzoin (*Ber.*, 1893, **26**, 2453), ga m. p. 98°.

On oxidation as before, a mixture of benzoic and *o*-nitrobenz acids was produced, from which the latter was obtained pure sublimation of the benzoic acid.

2-Nitrobenzil was nitrated in a similar way to the 3-isomer with fuming nitric acid (*d* 1·5), and the product from 1 g. yiel

·5 g. of pure 3 : 2′-dinitrobenzil, m. p. 149°, and a smaller amount f 2 : 2′-dinitrobenzil, m. p. 208°, after fractional crystallisation rom acetone.

Nitration of 4-Nitrobenzil: Preparation of 3 : 4′- and 2 : 4′-Dinitrobenzils.—The best method of preparing 3 : 4′- and 2 : 4′-dinitrobenzils in quantity is by the nitration of pure 4-nitrobenzil, ince a product is obtained which contains little besides these two someride and is consequently much easier to crystallise fractionally han the more complicated mixture of isomerides obtained by linitration and subsequent oxidation of benzoin or acetylbenzoin.

A solution of 13 g. of 4-nitrobenzil in 26 g. of fuming nitric acid *d* 1·5) was slowly heated and finally boiled gently for 15 minutes. t was then poured on ice. The yellow semi-solid product, which ardened after being washed with boiling water, drained, and dried, ras powdered and extracted with insufficient boiling chloroform ompletely to dissolve it. The small residue, on repeated crystallisation, yielded only 3 : 4′-dinitrobenzil, m. p. 137°. thus showing that o 4 : 4′-dinitrobenzil had been formed in the nitration, for this someride is much less soluble in chloroform than any other that ould have been present.

The chloroform extract, when rapidly cooled, deposited deep ellow, compact crystals of the unstable polymorph of 3 : 4′-dinitroenzil fairly free from 2 : 4′-dinitrobenzil. The processes of solution n chloroform and rapid cooling were repeated till the m. p. of the roduct, after one crystallisation from acetic acid, was 137°, showing t to be quite pure. The chloroform mother-liquors were diluted with lcohol and the mixture of 3 : 4′- and 2 : 4′-dinitrobenzils precipitated was further fractionally crystallised from chloroform; ventually a product was obtained so rich in 2 : 4′-dinitrobenzil hat crystals of this substance, which is much paler in colour than he 3 : 4′-isomeride, could be seen to separate when the chloroform olution was cooled.

Pure 2 : 4′-dinitrobenzil was obtained from the residue, after partial eparation of the 3 : 4′-isomeride as just described, by dissolving t in boiling acetic acid, cooling the solution carefully so that no rystals separated, and inoculating it with a crystal of this isomeride. he first crop of crystals, consisting largely of 2 : 4′-dinitrobenzil, as rapidly filtered off and recrystallised from acetic acid. When he amount of 2 : 4′-isomeride in the residues had been diminished, a urther quantity of 3 : 4′-dinitrobenzil was removed by fractional rystallisation from chloroform. By using the two methods lternately, the crude nitration product from 13 g. of 4 nitrobenzil as separated into 7·4 g. of pure 3 : 4′-dinitrobenzil, 1·7 g. of pure : 4′-dinitrobenzil, and a small residue.

Long Interaction of Benzoin and Acetylbenzoin with Fuming Nitric Acid.—A solution of 20 g. of benzoin in 60 g. of nitric acid (*d* 1·5) was kept at 25—30° for 6 hours and then poured on ice. The yellow gummy product was removed and boiled with 60 g. of nitric acid (*d* 1·4) and when nitrous fumes were no longer given off the solution was poured on ice. The bright yellow viscid mass which separated was well washed with boiling water, drained, and recrystallised from acetone; it then yielded 4 g. of 3 : 4′-dinitrobenzil, m. p. 137°.

The acetone mother-liquor was concentrated, and the crystals obtained, which were seen to be of more than one kind, were removed, powdered, and extracted with boiling chloroform; the residue when recrystallised from acetic acid, yielded 0·2 g. of 4 : 4′-dinitrobenzil, m. p. 213°. (A more complete investigation of this compound being in progress, its description is reserved.) The mother-liquor deposited on concentration 0·5 g. of 3 : 2′-dinitrobenzil, m. p. 149°.

When the chloroform extract (see above) was cooled, the first crop of crystals to separate consisted entirely of the 3 : 4′-isomeride; these were filtered off and the mother-liquor deposited a second crop containing crystals of 2 : 4′-dinitrobenzil as well. Pure 2 : 4′-dinitrobenzil (0·5 g.), m. p. 135°, was obtained by recrystallisation of the second crop from acetic acid.

Acetylbenzoin under similar conditions of nitration, followed by oxidation, yielded a similar mixture of the same isomeric dinitrobenzils, which were separated by identical methods.

Polymorphism and Oxidation of 3 : 4′-*Dinitrobenzil* (IV).—3 : 4′-*Dinitrobenzil* is soluble in boiling alcohol, more easily soluble in boiling acetic acid, acetone, chloroform, and benzene. It can be obtained in two polymorphic forms; the unstable form is deposited on chilling a chloroform solution or by seeding supersaturated solutions in other solvents with the unstable form, as deep yellow, rhombic crystals which become opaque when heated to 100°, or if allowed to remain for very long periods at the ordinary temperature, and change into the stable form. The latter usually crystallises at once when solutions in alcohol, acetic acid or acetone are cooled, as tufts of pale yellow, irregularly formed needles or elongated plates, similar in appearance to the 3 : 3′-isomeride but rather deeper in colour. The m. p. of the stable form is 137°; the unstable form, if rapidly heated, melts at 127°, sets again at once, and finally melts at 136—137° (Found: N, 9·25. $C_{14}H_8O_6N_2$ requires N, 9·3%).

5 G., oxidised by the method previously employed, yielded 5 g. of a mixture of *m*- and *p*-nitrobenzoic acids, which were separated by taking advantage of the greater solubility of the former in chloroform and of the sparing solubility of its barium salt. 2 G. of

-nitrobenzoic acid, m. p. 235°, and 1 g. of *m*-nitrobenzoic acid, ı. p. 141°, were obtained (the m. p.'s of mixtures of these acids ith authentic samples showed no depression).

3 : 4′ - *Dinitrobenzilmonophenylhydrazone*. — When equivalent mounts of the dinitrobenzil and phenylhydrazine were boiled ogether for a few minutes in alcohol, the *hydrazone* separated in ood yield ; it crystallised from alcohol as a mass of orange-coloured, elted needles, m. p. 182°, very soluble in boiling acetic acid (Found : N, 14·4. $C_{20}H_{14}O_5N_4$ requires N, 14·4%). It appeared to be a ingle individual, but no evidence was obtained to show which keto-roup condenses with the phenylhydrazine.

The *osazone* can be obtained by boiling the dinitrobenzil or its ıonohydrazone with a great excess of phenylhydrazine and phos-horic oxide in acetic acid solution. It is sparingly soluble in acetic cid and crystallises from acetic anhydride in orange-red, rhombic lates, m. p. 287° (decomp.) (Found: N, 17·3. $C_{26}H_{20}O_4N_6$ equires N, 17·5%).

2-m-*Nitrophenyl*-3-p-*nitrophenylquinoxaline* crystallises from oiling acetic acid in small, colourless plates, m. p. 221° (Found : N, 15·0. $C_{20}H_{12}O_4N_4$ requires N, 15·1%).

Oxidation of 2 : 4′-*Dinitrobenzil* (V).—2 : 4′-*Dinitrobenzil* appears o be slightly more soluble in acetone and chloroform than the : 4′-isomeride, but otherwise closely resembles it in solubility in hese and other solvents. It crystallises well from acetone or acetic cid in well-formed, pale yellow needles, m. p. 135°, which are photo-ropic and turn green when exposed to sunlight (Found : N, 9·1%).

1 G. yielded on oxidation 0·4 g. of *p*-nitrobenzoic acid, m. p. 235°, nd 0·2 g. of *o*-nitrobenzoic acid, m. p. 143°, which were separated y fractional crystallisation from water.

Isomeric Monophenylhydrazones of 2 : 4′-*Dinitrobenzil*.—When : 4′-dinitrobenzil was boiled for a few minutes with an equivalent mount of phenylhydrazine in alcohol there separated a mixture of range-coloured and yellow crystals. The latter were the less soluble nd were obtained pure by recrystallisation from boiling acetic acid s bright yellow needles, m. p. 224° (Found : N, 14·5. $C_{20}H_{14}O_5N_4$ equires N, 14·4%).

The orange-coloured substance, being the denser, was separated y agitating the mixture with alcohol and pouring off the suspension f the yellow substance. From solution in boiling acetic acid it rystallised in four-sided plates or flattened prisms, m. p. 201° Found : N, 14·3%).

The two substances appear to correspond to the two possible tructures $(o)NO_2\cdot C_6H_4\cdot C(:N\cdot NHPh)\cdot CO\cdot C_6H_4\cdot NO_2(p)$ and

$$(o)NO_2\cdot C_6H_4\cdot CO\cdot C(:N\cdot NHPh)\cdot C_6H_4\cdot NO_2(p),$$

but no evidence on which to assign the structures more exactly was obtained.

2-o-*Nitrophenyl*-3-p-*nitrophenylquinoxaline* crystallised from boiling acetic acid, in which it is easily soluble, in small, well-shaped, colourless needles, m. p. 186° (Found: N, 15·1. $C_{20}H_{12}O_4N_4$ *requires* N, 15·1%).

Derivatives of 2 : 2′- *and* 2 : 3′-*Dinitrobenzil*.—The monophenylhydrazone of the former compound is formed only slowly when the diketone is boiled with an excess of phenylhydrazine in alcoholic or acetic acid solution. It crystallises from boiling acetic acid, in which it is fairly readily soluble, in large, deep yellow, octahedral crystals, m. p. 199° (Found: N, 14·3. $C_{20}H_{14}O_5N_4$ requires N, 14·4%).

2 : 3′-*Dinitrobenzilmonophenylhydrazone*,

$$(o)NO_2{\cdot}C_6H_4{\cdot}C(:N{\cdot}NHPh){\cdot}CO{\cdot}C_6H_4{\cdot}NO_2(m)$$

or $(o)NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}C(:N{\cdot}NHPh){\cdot}C_6H_4{\cdot}NO_2(m)$, separates gradually on prolonged boiling of 2 : 3′-dinitrobenzil with an excess of phenylhydrazine in alcoholic solution. The product appears to be a single individual, crystallising from acetic acid, in which it is fairly readily soluble, in deep yellow prisms, m. p. 193° (decomp.) (Found: N, 14·3%).

2-m-*Nitrophenyl*-3-o-*nitrophenylquinoxaline* crystallises from boiling acetic acid in small, colourless or very pale yellow, rhombic prisms m. p. 168° (Found: N, 15·2. $C_{20}H_{12}O_4N_4$ requires N, 15·1%).

THE QUEEN'S COLLEGE, OXFORD. [*Received, October 20th, 1927.*]

CXXXVIII.—*The Condensation of Chloral with Substituted Phenols.*

By FREDERICK DANIEL CHATTAWAY and FERNANDO CALVET.

PHENOLS have been found to condense with aldehydes in three characteristic ways:

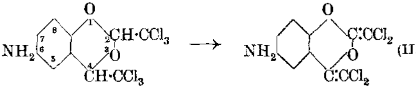
(1) The phenol (1 mol.) unites with the aldehyde (1 mol.), the condensation being of the aldol type.

(2) The phenol (2 mols.) reacts with the aldehyde (1 mol.), water (1 mol.) being eliminated and a dihydroxy-derivative of diphenylmethane or closely related hydrocarbon produced.

(3) The aldehyde (2 mols.) condenses with the phenol (1 mol.), subsequent elimination of water leading to the formation of a heterocyclic compound. For example, chloral reacts thus with *p*-nitrophenol (Chattaway, J., 1926, 2720), *p*-hydroxybenzoic acid (Chattaway and Calvet, J., 1927, 685), and phenol-*p*-sulphonic acid (Chattaway and Morris, J., 1927, 2013) in presence of concentrated sulphuric acid, yielding derivatives of 1 : 3-benzdioxin.

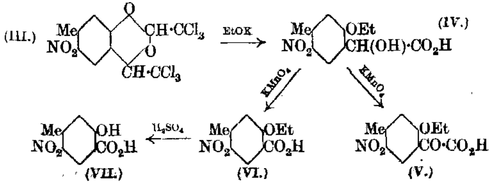
Several other *p*-substituted phenols react with chloral in a similar way. For example, *p*-aminophenol in presence of concentrated sulphuric acid readily gives 6-amino-2 : 4-bistrichloromethyl-1 : 3-benzdioxin (I), identical with the reduction product from 6-nitro-2 : 4-bistrichloromethylbenzdioxin (Chattaway, J., 1926, 2722, 2725, where the two substances are named as derivatives of ethylbenzene).

The action of alcoholic potash does not break this compound down so completely as it does the similarly constituted 6-nitro- and 6-carboxy-compounds, two molecules only of hydrogen chloride being eliminated and *6-amino-2 : 4-bisdichloromethylene-1 : 3-benzdioxin* (II) formed.

(I.)  (II.)

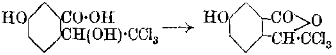
Azophenols also react similarly; for example, *p*-tolueneazophenol yields *6-*p*-tolueneazo-2 : 4-bistrichloromethyl-1 : 3-benzdioxin* (formula as I), the constitution of which has been established by reducing it in alcoholic solution with stannous chloride to *p*-toluidine and 6-amino-2 : 4-bistrichloromethylbenzdioxin (I).

o-Nitro-*m*-cresol condenses similarly with chloral in presence of concentrated sulphuric acid and forms *6-nitro-7-methyl-2 : 4-bistrichloromethyl-1 : 3-benzdioxin* (III), showing that the presence of a methyl group in a position meta to the phenolic hydroxyl does not interfere with the reaction. The constitution of this compound is shown by its behaviour with alcoholic potash: *5-nitro-2-ethoxy-4-methylmandelic acid* (IV) is formed, which on oxidation by potassium permanganate yields a mixture of *5-nitro-2-ethoxy-*p*-tolylglyoxylic acid* (V) and *6-nitro-3-ethoxy-*p*-toluic acid* (VI); the latter on hydrolysis of the ethoxy-group yields 6-nitro-3-hydroxy-*p*-toluic acid (VII) identical with the product obtained by the nitration of 3-hydroxy-*p*-toluic acid:



Salicylic acid and both *o*- and *m*-nitrophenol, where the position para to the hydroxyl group is open, also condense with chloral in presence of concentrated sulphuric acid, possibly by the introduction of a $-CH(OH)\cdot CCl_3$ group in the vacant para-position, but in each case a viscid and resin-like uncrystallisable product has been obtained.

That the $-CH(OH)\cdot CCl_3$ group enters the unoccupied para-position in these reactions is rendered more probable by the circumstance that when the adjacent meta-position is occupied by a group with which it can react, well-crystallised condensation products are formed; *e.g.*, *m*-hydroxybenzoic acid gives 5-hydroxytrichloromethylphthalide (Fritsch, *Annalen*, 1897, **296**, 344).



Even by using a large excess of chloral (2 mols.) it has been found impossible to introduce another $-CH(OH)\cdot CCl_3$ group into the molecule, the reason probably being that its introduction is such a slow process that before any recognisable amount has been introduced the chloral itself polymerises to metachloral under the influence of the sulphuric acid.

5-Nitrosalicylic acid, *p*-nitro-*o*-cresol, and 2 : 4-dinitrophenol, in all of which one position ortho to the hydroxyl group is occupied do not condense with chloral in presence of concentrated sulphuric acid. This may be due to the steric hindrance of the substituents ortho to the phenolic group preventing the addition which probably precedes the entrance of the $-CH(OH)\cdot CCl_3$ group into the nucleus

EXPERIMENTAL.

6-*Amino*-2 : 4-*bistrichloromethyl*-1 : 3-*benzdioxin* (I).—To a solution of 70 g. of *p*-aminophenol hydrochloride in 800 c.c. of concentrated sulphuric acid, cooled with ice-water, 250 g. of chloral hydrate were added. The mixture was well shaken for ½ hour and, after 3 days, poured into 2500 c.c. of water containing ice The brown solid that separated was recrystallised (yield, 98 g from much boiling water, in which it was sparingly soluble, and was then washed with a little alcohol, which dissolved a small quantity of adhering tarry matter. The residual mixture of 6-amino-2 : 4-bistrichloromethylbenzdioxin sulphate and *p*-aminophenol-*o*-sulphonic acid was finely powdered and poured into 100 c.c. of water, to which a solution of sodium hydroxide was added until an alkaline reaction was obtained; the sodium aminophenolsulphonate remained in solution. The precipitated condensation product

(45 g.), after being recrystallised from alcohol, melted at 174·5° and proved to be identical with the amino-compound obtained by reduction of 6-nitro-2 : 4-bistrichloromethylbenzdioxin (Chattaway, *loc. cit.*), giving the same acetyl derivative, m. p. 206°. Its identity with the latter compound was further established by converting it into the corresponding 6-carboxylic acid by replacing the amino-group by carboxyl, through the cyano-derivative.

From the alkaline solution, on acidification with acetic acid, *p*-aminophenol-*o*-sulphonic acid crystallised in very small needles, which were recrystallised from water (8·5 g.) (Found: C, 38·6; H, 3·7; N, 7·6; S, 16·6. Calc. for $C_6H_7O_4NS$: C, 38·1; H, 3·7; N, 7·4; S, 16·9%) (compare Post, *Annalen*, 1880, **205**, 49).

7-Bromo-6-amino-2 : 4-bistrichloromethyl-1 : 3-benzdioxin.—The base (4·2 g.) and bromine (30 c.c. of a solution of 160 g. per litre) were boiled in glacial acetic acid for a few seconds. (Longer heating causes further bromination.) The *monobromo*-compound, which crystallised on cooling, was obtained, after several crystallisations from alcohol, in well-formed, colourless needles, m. p. 171—173° (yield, 2 g.). *It is insoluble in light petroleum, but fairly readily* soluble in ether, alcohol and acetic acid (Found: Cl, 46·3; Br, 17·4. $C_{10}H_6O_2NCl_6Br$ requires Cl, 45·8; Br, 17·2%).

The monobromo-compound yielded an *acetyl* derivative when it was boiled for 10 minutes with a mixture of acetic anhydride and acetyl chloride. The product was twice recrystallised from boiling alcohol, in which it was moderately easily soluble, and from which it separated in small, colourless plates, m. p. 231—232·5° (Found: Cl, 42·8; Br, 16·1. $C_{12}H_8O_3NCl_6Br$ requires Cl, 42·2; Br, 15·8%).

6-Amino-2 : 4-bisdichloromethylene-1 : 3-benzdioxin (II).—The finely *powdered base (I) (30 g.) was slowly added to a boiling solution* of 80 g. of potassium hydroxide in 400 c.c. of alcohol and further boiled for ½ hour. To the boiling liquid 400 c.c. of hot water were added and the alcohol was distilled off in steam. On cooling, the heavy oily product solidified. After being recrystallised three times from hot alcohol (yield, 17 g.) it was obtained in small, colourless needles, m. p. 113—117°. It is easily soluble in alcohol, ether, chloroform, carbon tetrachloride, and carbon disulphide (Found: C, 37·8; H, 1·4; N, 4·5; Cl, 45·2. $C_{10}H_5O_2NCl_4$ requires C, 38·3; H, 1·6; N, 4·5; Cl, 45·4%). It can be kept for a considerable time without change, though after some months it becomes tarry. When dissolved *in carbon tetrachloride it* combines directly with bromine without evolution of hydrogen bromide and thus appears to be an unsaturated compound.

When added to acetic anhydride containing a drop of con-

centrated sulphuric acid, it readily formed an *acetyl* derivative which crystallised from dilute, boiling alcohol in microscopica needles, m. p. 191—194° (Found: Cl, 40·0. $C_{12}H_7O_3NCl_4$ require: Cl, 40·0%).

6-p-*Tolueneazo-2 : 4-bistrichloromethyl-1 : 3-benzdioxin* (formul as I).—A solution of 20 g. of *p*-tolueneazophenol and 40 g. of chl ra hydrate in 300 c.c. of concentrated sulphuric acid was kept fo 3 days with frequent shaking, a small quantity of the condensat or product separating, and was then poured into 1000 c.c. of col water. The red product dissolved readily in boiling alcohol, an separated in reddish-yellow needles (10 g.), m. p. 152—153°. It i easily soluble in ether, alcohol, and acetic acid (Found: Cl, 43·4 N, 5·7. $C_{17}H_{12}O_2N_2Cl_6$ requires Cl, 43·5; N, 5·7%).

Reduction. 4 G. of the finely powdered substance and 10 g. o stannous chloride were added to 100 c.c. of alcohol, and the liqui was boiled under reflux for 5 minutes, its colour being totall discharged. The liquid was made slightly acid with dilute hydro chloric acid, the alcohol distilled off in steam, and the aqueou liquid cooled and extracted with ether. The extract was con centrated to a small volume and steam-distilled; *p*-toluidine cam over, and was identified by means of its acetyl derivative.

The solid remaining in the flask, after being recrystallised fro alcohol, was identified as 6-amino-2 : 4-bistrichloromethylbenz dioxin, giving the already described acetyl derivative. The yiel was 2·3 g.

5-*Hydroxytrichloromethylphthalide.*—When a solution of 13 g (1 mol.) of *m*-hydroxybenzoic acid and 33 g. (2 mols.) of chlora hydrate in 100 c.c. of concentrated sulphuric acid was kept fo 2 days, the condensation product crystallised in fine needles, mixe with metachloral. The liquid was poured into 500 c.c. of ice water and the phthalide which separated was extracted with ho alcohol and recrystallised several times from this solvent; m. p 199—200° (compare Fritsch, *loc. cit.*) (Found: Cl, 39·8. Calc. fo $C_9H_5O_3Cl_3$: Cl, 39·75%).

6-*Nitro-7-methyl-2 : 4-bistrichloromethyl-1 : 3-benzdioxin* (III).—The condensation was effected as in the preceding case (19 g. o *p*-nitro-*m*-cresol [1 mol.]; 41 g. of chloral hydrate [2 mols.]; 20 c.c. of concentrated sulphuric acid; 800 g. of crushed ice). Th solid that separated was washed with a few c.c. of boiling alcoho which removed a little tar, and crystallised several times fro alcohol (animal charcoal), being obtained in very slightly yello needles, m. p. 148—150° (Found: Cl, 49·8. $C_{11}H_7O_4NCl_6$ requir Cl, 49·5%).

5-Nitro-2-ethoxy-4-methylmandelic Acid (IV).—10 G. of finely powdered 6-nitro-7-methyl-2 : 4-bistrichloromethylbenzdioxin were added to a cooled solution of 14 g. of potassium hydroxide (9 mols.) in 100 c.c. of alcohol. The reaction proceeds with evolution of heat, and the temperature must not be allowed to rise. The liquid was boiled for just 3 minutes on the water-bath, 100 c.c. of hot water were added, and after partial neutralisation with dilute hydrochloric acid, the alcohol was distilled off in steam. On allowing the aqueous liquid to cool (and after separating by filtration a considerable amount of tarry matter which came down first) *5-nitro-2-ethoxy-4-methylmandelic acid* was obtained as a voluminous mass of very small needles (3·2 g.). After being recrystallised three times from water, it melted at 155°. It is very soluble in boiling water and alcohol, moderately easily soluble in ether, but insoluble in low-boiling petroleum (Found: C, 51·6; H, 5·3; N, 5·5. $C_{11}H_{13}O_6N$ requires C, 51·8; H, 5·1; N, 5·5%).

*Preparation of 5-Nitro-2-ethoxy-*p*-tolylglyoxylic Acid* (V) *and 6-Nitro-3-ethoxy-*p*-toluic Acid* (VI).—An alkaline solution of 5 g. of the mandelic acid in sodium carbonate was heated on the water-bath, and 11 g. of potassium permanganate were slowly added, the colour of which was discharged after 10 minutes' heating. The filtrate from the manganese dioxide (which was washed with hot water), on cooling, was made acid with dilute hydrochloric acid; the product which then crystallised (1·9 g.) was a mixture of very small prisms and minute needles. The latter dissolved in boiling benzene (30 c.c.), and on cooling, the solution deposited *6-nitro-3-ethoxy-*p*-toluic acid* (VI), m. p. 166° after twice crystallising from water (yield, 0·7 g.). It is easily soluble in ether and benzene but insoluble in low-boiling petroleum (Found: C, 53·6; H, 4·8; N, 6·3. $C_{10}H_{11}O_5N$ requires C, 53·3; H, 4·9; N, 6·2%).

The prisms (1 g.) left undissolved by the boiling benzene crystallised from boiling water in colourless plates, m. p. 194°. From its analysis and the fact that it gives a well-defined phenylhydrazone the substance is shown to be *5-nitro-2-ethoxy-*p*-tolylglyoxylic acid* (V) (Found: C, 52·5; H, 4·4; N, 5·6. $C_{11}H_{11}O_5N$ requires C, 52·2; H, 4·3; N, 5·5%).

The *phenylhydrazone* separated in yellow needles when an alcoholic solution of the ketonic acid was boiled for 15 minutes with a small excess of phenylhydrazine. After crystallising three times from alcohol, in which it was easily soluble, it melted at 199° (Found: N, 12·3. $C_{17}H_{17}O_5N_3$ requires N, 12·2%).

*Hydrolysis of the Ethoxy-group of 6-Nitro-3-ethoxy-*p*-toluic Acid.*—A solution of 0·5 g. of the acid in 5 c.c. of concentrated sulphuric

acid was heated for 3 hours on a water-bath and poured into 30 c.c. of water. The 6-nitro-3-hydroxy-*p*-toluic acid (VII) that separated, after being recrystallised from a few c.c. of water, was obtained in very slightly yellow needles (0·25 g.), m. p. 225°, identical with the acid described below (Found: N, 7·3. Calc. for $C_8H_7O_5N$: N, 7·1%).

*The Nitration of 3-Hydroxy-*p*-toluic Acid.*—We have not been able to obtain a fully nitrated product by Borsche and Berkhout's method (*Annalen*, 1903, **330**, 101). The following method is satisfactory.

To a vigorously stirred suspension of 10 g. of 3-hydroxy-*p*-toluic acid in 50 c.c. of glacial acetic acid, a mixture of 10 c.c. of nitric acid (*d* 1·5) and 10 c.c. of acetic acid was added. The temperature rose to about 60—70°, and the toluic acid dissolved completely. After cooling, the whole was poured into 400 c.c. of cold water, and the solid which separated was recrystallised from boiling water (yield, 5 g.). The nitrohydroxy-*p*-toluic acid (VII) was thus obtained in very pale yellowish needles, m. p. 225°, melting somewhat higher than the product described by Borsche and Berkhout (Found: N, 7·2%).

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CXXXIX.—*Imide Ring Closure in Derivatives of Diketosuccinic Acid Phenylosazone.*

By FREDERICK DANIEL CHATTAWAY and WILLIAM GERALD HUMPHREY.

ALTHOUGH diketosuccinic anhydride phenylosazone has been long known, its properties have been little studied, the products of its reduction only having been described (J., 1927, 2133). In the present paper, the formation of derivatives containing the imide ring by the action of ammonia, primary amines, and α-hydrazines upon this anhydride is described.

Diketosuccinimide phenylosazone (I) is most readily prepared by fusing the anhydride with urea. It is very stable, being unchanged by prolonged boiling with hydrochloric acid, although it dissolves in boiling aqueous sodium hydroxide, liberating ammonia and forming sodium diketosuccinate phenylosazone (II), which is at once converted by acids into 4 : 5-diketo-1-phenylpyrazoline-3-carboxylic acid 4-phenylhydrazone (III).

Benzylamine combines at once with diketosuccinic anhydride phenylosazone if the latter is suspended in ether, the *benzylamine* salt of *diketosuccinobenzylamic acid phenylosazone* (IV) being formed. The base is readily removed and the anhydride re-formed by heating with acetic anhydride, and acidification causes the formation of the corresponding imide, diketosuccinobenzylimide phenylosazone (V). Dibenzylamine reacts in a similar manner, forming the *salt* of the diketosuccinodibenzylamic acid, from which acids liberate one molecule of the base, yielding *diketosuccinodibenzylamic acid phenylosazone*, imide formation not being here possible and the base preventing, as in the former case, the pyrazoline ring closure.

Aniline reacts with the anhydride to yield a mixture of *diketosuccinanilic acid phenylosazone* (VI) and *diketosuccinanil phenylosazone* (VII). By prolonged boiling with aniline, the former is converted into the latter, the yield of which consequently increases with the time of heating. Since, however, decomposition occurs during prolonged heating at this high temperature, it is advisable to boil for a short time only and to separate the mixture of anilic acid and anil. The former is converted by prolonged boiling with aqueous-alcoholic hydrochloric acid into the pyrazoline derivative (III).

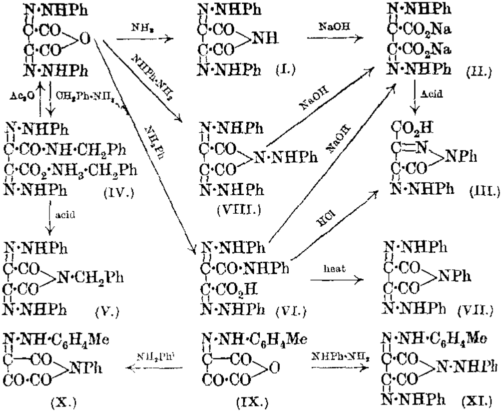
The anhydride is unaffected by prolonged fusion with tribenzylamine or with diphenylamine.

The anhydride reacts with phenylhydrazine in hot or cold acetic acid solution to yield a corresponding imide derivative, *diketosuccinophenylhydrazide phenylosazone* (VIII). *as*-Phenylmethylhydrazine acts similarly. No intermediate product could be isolated in either case and it therefore seems probable that both hydrazides are of the α-variety.

Analogous derivatives of certain substituted phenylhydrazones and osazones of diketosuccinic anhydride have also been prepared. The tolylhydrazones (IX) (J., 1927, 2793) yield with aniline the corresponding *anils* (X), the ketonic group remaining unchanged. Phenylhydrazine acts upon the ketonic group as well as forming the *hydrazide* (XI). The 2 : 4-dichloro- and 2 : 4-dibromo-anhydrides (J., 1927, 1323) react with aniline less readily, the products consisting entirely of the corresponding *anils*.

All the above compounds which contain the succinimide ring are, like the parent substance, very stable towards acids, but are converted by boiling 10% sodium hydroxide solution into sodium diketosuccinate phenylosazones.

The following scheme represents the main reactions :



EXPERIMENTAL.

Diketosuccinimide phenylosazone (I) was prepared by fusing gently for 10 minutes a mixture of 5 g. of diketosuccinic anhydride phenylosazone and 50 g. of urea. The pasty, orange-yellow product when cold, was powdered, extracted with hot water to remove urea and biuret, and crystallised from alcohol, in which it was rather sparingly soluble, separating in orange-yellow, long plates or thin prisms, m. p. 189° (Found: C, 62·5; H, 4·2; N, 22·8. $C_{16}H_{13}O_2N_5$ requires C, 62·8; H, 4·3; N, 22·8%).

The *benzylamine* salt of *diketosuccinobenzylamic acid phenylosazone* (IV) was prepared by adding 4 c.c. of benzylamine (excess) to a fine suspension of 3 g. of the anhydride in 30 c.c. of ether. The red anhydride was slowly converted into a yellow pulp of the *benzylamine* salt, which was filtered off and washed with ether. It crystallised from acetone, in which it was rather sparingly soluble, in light yellow, hair-like needles, m. p. 165° (decomp.) (Found: C, 68·8; H, 5·7; N, 15·95. $C_{30}H_{30}O_3N_6$ requires C, 68·9; H, 5·7; N, 16·1%).

Diketosuccinobenzylimide phenylosazone (V) was obtained from the above benzylamine salt by crystallisation from acetic acid, by the addition of hydrochloric acid to its alcoholic solution.

rystallised from alcohol, in which it was rather sparingly soluble, n orange-yellow, rhombic plates, m. p. 179° (Found: N, 17·6. $_{23}H_{19}O_2N_5$ requires N, 17·6%).

The *dibenzylamine* salt of *diketosuccinodibenzylamic acid phenylsazone*, $(CH_2Ph)_2N{\cdot}CO{\cdot}C(:N{\cdot}NHPh){\cdot}C(:N{\cdot}NHPh){\cdot}CO_2NH_2(CH_2Ph)_2$, as prepared in a similar manner to the corresponding benzylamine ompound. It crystallised from alcohol, in which it was very oluble, in light yellow, hair-like needles, m. p. 161—162° (decomp.) Found: N, 11·85. $C_{44}H_{42}O_3N_6$ requires N, 11·95%).

Diketosuccinodibenzylamic acid phenylosazone,

$$(CH_2Ph)_2N{\cdot}CO{\cdot}C(:N{\cdot}NHPh){\cdot}C(:N{\cdot}NHPh){\cdot}CO_2H,$$

as obtained from the above salt by the addition of hydrochloric cid to its alcoholic solution. It crystallised from alcohol, in which was moderately easily soluble, in orange-yellow, flattened prisms, . p. 180° (Found: N, 13·9. $C_{30}H_{27}O_3N_5$ requires N, 13·9%).

Diketosuccinanilic Acid Phenylosazone (VI).—When 2 g. of the nhydride were boiled for 10 minutes with 40 c.c. of aniline, a lear dark reddish-brown solution was obtained from which *diketouccinanilic acid phenylosazone* separated on cooling. It was filtered ff, washed with alcohol, and recrystallised from alcohol, in which was rather sparingly soluble, separating in very small, orangeellow, fine prisms, m. p. 201° (decomp.) (Found: C, 65·6; H, ·6; N, 17·25. $C_{22}H_{19}O_3N_5$ requires C, 65·8; H, 4·7; N, 17·45%).

This compound crystallises from acetic acid, in which it is very oluble, in glistening, orange-yellow, long plates, containing one olecule of acetic acid, which melt between 135° and 200° according o the rate of heating. The crystals must be dried on a porous lass filter in a current of air; they lose acetic acid slowly on heating elow 100°, and on being washed with alcohol or ether they fall to fine powder of the pure compound (m. p. 201°, decomp.) (Found: ss after heating at 130°, 13·1. $C_{22}H_{19}O_3N_5,C_2H_4O_2$ requires loss, 3·0%).

Diketosuccinanil phenylosazone (VII) slowly separated as a felted ass of orange-red, slender prisms when the aniline mother-liquor om the above preparation was diluted with about 150 c.c. of lcohol. It crystallised from acetic acid, in which it was moderately asily soluble, in orange-red, long, slender prisms, m. p. 252° lecomp.) (Found: C, 69·1; H, 4·5; N, 18·1. $C_{22}H_{17}O_2N_5$ requires , 68·9; H, 4·4; N, 18·3%).

Diketosuccinophenylhydrazide phenylosazone (VIII) was formed by he action of phenylhydrazine upon the anhydride in acetic acid spension, slowly in the cold but almost instantaneously on heating. he *hydrazide*, which separated in felted, fine prisms on cooling, ystallised from acetic acid, in which it was moderately easily

soluble, in orange-yellow, thin prisms, m. p. 270° (decomp.) (Found C, 66·1; H, 4·55; N, 21·1. $C_{22}H_{18}O_2N_6$ requires C, 66·3; H, 4·5; N, 21·1%).

Diketosuccinophenylmethylhydrazide phenylosazone (formula as VIII) was prepared in the same manner by the action of phenylmethylhydrazine upon the anhydride. It crystallised from acetic acid, in which it was moderately easily soluble, in bright yellow, fine prisms, m. p. 243·5° (decomp.) (Found: N, 20·5. $C_{23}H_{20}O_2N_6$ requires N, 20·4%).

Diketosuccinanil p-*tolylhydrazone* (X) was obtained by boiling 2 g. of diketosuccinic anhydride *p*-tolylhydrazone (IX) with 10 c.c. of aniline for a minute. A very dark red solution was obtained which, after being cooled and diluted with 40 c.c. of ether, slowly deposited the *anil*. This crystallised from alcohol, in which it was sparingly soluble, in yellow, rhombic plates, m. p. 199° (decomp.) (Found: C, 66·6; H, 4·5; N, 13·7. $C_{17}H_{13}O_3N_3$ requires C, 66·4; H, 4·2; N, 13·8%).

Diketosuccinophenylhydrazide o-*tolylphenylosazone* (XI) was prepared by heating 2 g. of diketosuccinic anhydride o-tolylhydrazone with 3 g. of phenylhydrazine in acetic acid solution. It crystallised from acetic acid, in which it was moderately easily soluble, in orange-yellow, fine prisms, m. p. 250° (decomp.) (Found: N, 20·5. $C_{23}H_{20}O_2N_6$ requires N, 20·4%).

Diketosuccinanil 2 : 4-*dichlorophenylosazone* (formula as VII) was prepared by boiling the corresponding anhydride with aniline. It crystallised from acetic acid, in which it was sparingly soluble, in orange-yellow, hair-like needles, m. p. 308° (decomp.) (Found: Cl, 27·1. $C_{22}H_{13}O_2N_5Cl_4$ requires Cl, 27·25%).

Diketosuccinanil 2 : 4-*dibromophenylosazone*, prepared in the same manner, crystallised from acetic acid, in which it was sparingly soluble, in orange, hair-like needles, m. p. 309° (decomp.) (Found: Br, 45·8. $C_{22}H_{13}O_2N_5Br_4$ requires Br, 45·8%).

Diketosuccinophenylhydrazide 2 : 4-*dichlorophenylosazone* (formula as VIII) was prepared in the same manner as the unsubstituted compound from the corresponding anhydride. It crystallised from acetic acid, in which it was sparingly soluble, in deep yellow, hair-like needles, m. p. 280° (decomp.) (Found: Cl, 26·6. $C_{22}H_{14}O_2N_6Cl_4$ requires Cl, 26·5%).

Diketosuccinophenylhydrazide 2 : 4-*dibromophenylosazone*, which was similarly prepared, crystallised from acetic acid, in which it was sparingly soluble, in orange-yellow, hair-like needles, m. p. 295° (decomp.) (Found: Br, 44·8. $C_{22}H_{14}O_2N_6Br_4$ requires Br, 44·8%).

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CXL.—*The Action of Nitrous Acid on Amino-compounds. Part I. Methylamine and Ammonia.*

By Thomas Weston Johns Taylor.

As has been shown in a previous communication (Taylor, Wignall, and Cowley, J., 1927, 1923), aqueous solutions of nitrous acid can be considerably stabilised if the concentration is below a critical value which depends on the temperature and pressure, and if the solution is covered by a layer of " medicinal paraffin."

A preliminary study of the conditions of interaction of nitrous acid with simple aliphatic amino- and amido-compounds showed that the phenomena were extremely diverse, and thus it was thought essential to investigate the case of methylamine and ammonia where the fewest possible complications are present.

Euler (*Annalen*, 1903, **330**, 280) made the important observation that in $0{\cdot}05N$-solution at 40°, methylamine nitrite is stable, but reacts readily with an equivalent of nitrous acid. He attempted to measure the rate of the reaction by the rate of evolution of nitrogen, but his results are inconclusive, largely because of the decomposition of the nitrous acid. Later workers (Neogi, J., 1914, **105**, 1270; Oddo and Cesaris, *Gazzetta*, 1914, **44**, ii, 209) seem to consider that the reaction is essentially the decomposition of the nitrite.

In the case of ammonia, the reaction has been regarded as the decomposition of the nitrite and investigated as such, principally by Arndt (*Z. physikal. Chem.*, 1901, **39**, 64; 1903, **45**, 570) and by Blanchard (*ibid.*, 1902, **41**, 681). The most important results obtained were that ammonium nitrite, although stable in solution at room temperature, decomposes freely at 60°. Arndt suggested that the rate of decomposition was proportional to the product $[NH_4NO_2][HNO_2]$, whilst Blanchard attributed a catalytic effect to the hydrogen ion and suggested that the velocity varied as the product $[H^{\cdot} + HNO_2][NH_4^{\cdot}][NO_2']$. Both followed the reaction by the rate of evolution of nitrogen, and the results of both, especially those from experiments in the presence of excess of mineral acid, were undoubtedly obscured by the spontaneous decomposition of the nitrous acid.

Plimmer (J., 1925, **127**, 2651) performed a few experiments on the action of large excess of nitrous acid on ammonia in the presence of acetic acid; his results indicate that the reaction is complete at 16° in 2½ hours.

Since the rate of gas evolution is an accurate measure of the velocity of reaction only if the solution is continuously and

thoroughly agitated, and since such agitation greatly increases the rate of decomposition of the nitrous acid, the velocity of reaction has been followed by estimating the concentration of undecomposed amine. Further, the initial concentration of nitrous acid was never greater than 0·15*N*, *i.e.*, well below the critical concentration (0·2*N*) under the conditions employed.

In a series of preliminary experiments, it was found that ammonia and methylamine show exactly the same type of behaviour towards nitrous acid, the velocity coefficient for the former being a little less than half of that for the latter. Thus methylamine is much more suitable for accurate investigation, since the side reaction, the decomposition of nitrous acid, forms a smaller fraction of the total reaction in any given time.

I. *Methylamine.*

Methylamine free from ammonia could only be obtained by Wallach's method from acetoxime (*Annalen*, 1900, **312**, 175, footnote). The hydrochloride was recrystallised three times from 96% alcohol and its purity established by determining the equivalent of the methylamine against standard sulphuric acid. The methylamine was used as an approximately 0·5*N* aqueous solution of the free base, which kept well in stoppered bottles. Nitrous acid was prepared from pure barium nitrite and sulphuric acid as in the previous communication, no attempt being made to remove the barium sulphate. All experiments were carried out at 25° ± 0·05°; the reaction mixture was covered by a layer of medicinal paraffin, and the stirrer passed through that layer, care being taken to avoid air bubbles being drawn into the solution. Samples of the solution were withdrawn by a pipette from time to time, and run into excess of pure aqueous caustic soda; the methylamine was at once distilled in steam into a known amount of standard acid; the accuracy of the method was found to be about ± 0·5%.

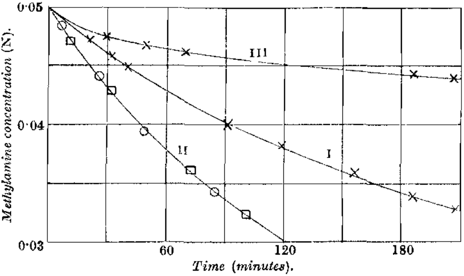
0·05N-*Methylamine* + 0·05N-*nitrous acid.* No change in the concentration of methylamine occurred during 2½ hours; this is in agreement with previous workers.

0·05N-*Methylamine* + 0·05N-*nitrous acid* + 0·05N-*sulphuric acid.* No reaction could be observed during a period of 2½ hours. Euler (*loc. cit.*), with the same concentrations at 40°, found a very slow reaction, but in his experimental data (40 c.c. of gas in 50 hours) he does not state what proportion of the gas was nitric oxide from the decomposition of the nitrous acid. At least half must have been nitric oxide, in which case the concentration of methylamine fell from 0·05*N* to 0·0496*N* in 50 hours.

0·05N-*Methylamine* + 0·1N-*nitrous acid*. A fairly rapid reaction occurs. The rate of this was measured repeatedly; some of the results are shown in the figure (Curve I). From the smooth curve drawn through them the values shown in Table I were read.

From the results obtained so far, it is clear that the reaction is one in which methylamine ions, nitrite ions, and free nitrous acid all take part. Estimation of the concentration of nitrous acid from time to time showed that one molecule of nitrous acid disappears for each molecule of methylamine, and not two; thus

FIG. 1.



Curve I. 0·05N-$CH_3{\cdot}NH_2$ + 0·1N-HNO_2.
Curve II. ⊙ 0·05N-$CH_3{\cdot}NH_2$ + 0·1N-HNO_2 + 0·05N-$CH_3{\cdot}NH_3Cl$.
▣ 0·05N-$CH_3{\cdot}NH_2$ + 0·1N-HNO_2 + 0·05N-$Ba(NO_3)_2$.
Curve III. 0·05N-$CH_3{\cdot}NH_2$ + 0·1N-HNO_2 + 0·05N-H_2SO_4.

the reaction velocity, assuming that it varies as the product $[CH_3{\cdot}NH_3^{\cdot}][NO_2'][HNO_2]$, should be given by an equation of the form $-dx/dt = kax^2$, where x is the concentration of methylamine (and hence of the nitrite ion) at time t, and a is the initial concentration of methylamine, and hence that of the undissociated nitrous acid, assuming it to be completely undissociated in the presence of the excess nitrite ion. Values of the coefficient k calculated for every 30 minutes are shown in Table I.

TABLE I.

t (mins.).	x.	k (min.$^{-1}$).	k corr. (min.$^{-1}$).	t (mins.).	x.	k (min.$^{-1}$).	k corr. (min.$^{-1}$).
0	0·0500	—	—	120	0·0381	1·04	1·12
30	0·0461	1·13	1·15	150	0·0361	1·03	1·13
60	0·0427	1·14	1·18	180	0·0343	1·02	1·13
90	0·0402	1·08	1·15				**Mean** 1·14

measurements at 25° with 0·05N-methylamine, 0·1N-nitrous acid, and 0·05N-sulphuric acid, which are shown in Curve III of the figure. At the start the mixture contains essentially methylamine ions, sulphate ions, nitrite ions, and nitrous acid; as the reaction proceeds methylamine disappears and highly dissociated sulphuric acid is formed; hence the hydrogen-ion concentration rises, the nitrite ion concentration falls, and the reaction becomes slower and slower. At time t the concentration of the hydrogen ions can be taken as $(a - x)$, and that of the undissociated nitrous acid as $(a + x)$; thus if the dissociation constant of nitrous acid is C, $[NO_2'] = C(a + x)/(a - x)$. Hence the equation for the reaction should be $-dx/dt = kCx(a + x)^2/(a - x)$, whence, integrating between the times t_1 and t_2,

$$kC = \left(\frac{1}{a}\log_e\frac{x_1}{x_2}\cdot\frac{a + x_2}{a + x_1} - \frac{2}{a + x_2} + \frac{2}{a + x_1}\right)\frac{1}{t_2 - t_1} \quad . \quad (3)$$

The expression obviously cannot be integrated back to time 0, since it only holds when the concentration of free sulphuric acid is appreciable. Values of kC calculated from (3) vary between 2×10^{-4} and 4×10^{-4} (min.$^{-1}$); the variation arises from three causes: (i) The reaction is proceeding very slowly in the region where the expression holds; (ii) expression (3) is extremely sensitive to small inaccuracies in the values of x_1 and x_2; (iii) no allowance is made for the spontaneous decomposition of nitrous acid.

Nevertheless, since k has been shown to be 1·14, the calculation gives a value for C which agrees in order of magnitude with that determined by Blanchard, 4×10^{-4}, and by Schumann, $4·5 \times 10^{-4}$ (Landolt–Börnstein " Tabellen," 5th Edn.).

II. *Ammonia.*

The reaction with ammonia was not examined in any detail. The following experimental facts were established: (i) Ammonia (0·05N) at 25° does not react with one equivalent of nitrous acid, but reacts with two, the velocity coefficient being of the order of 0·48 (normality^{-2}; min.$^{-1}$). (ii) The velocity is lowered by addition of mineral acids and of potassium chloride. (iii) The velocity is accelerated equally by equivalent quantities of either ammonium chloride or barium nitrite.

Hence there is little doubt that the same mechanism is involved and that the velocity varies as the product $[NH_4^{\cdot}][NO_2'][HNO_2]$, agreeing with the conclusions of Arndt; Blanchard's expression is erroneous and his attribution of a catalytic effect to the hydrogen ion obviously arose from adding small amounts of strong acid to

solutions of ammonium nitrite, whereby free nitrous acid was formed.

The results obtained may have one of two meanings. Either the reaction involves the two ions and a molecule of nitrous acid, or, since the concentration of any form of undissociated amine nitrite is proportional to the product of the concentrations of its ions, the actual reacting molecules may be undissociated molecules of amine nitrite and those of nitrous acid. The results suggest that the best conditions for converting an aliphatic amine into the alcohol are to use large excess of nitrous acid and to avoid the presence of mineral acids in the solution.

My thanks are due to Mr. J. F. Cowley for the help he has given me during the preliminary experiments.

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OXFORD. [*Received, February 27th*, 1928.]

CXLI.—*The Alkaloids of Some Indian Aconites* (A. Balfourii, A. deinorrhizum, *and "Chumbi Aconite"*).

By THOMAS ANDERSON HENRY and THOMAS MARVEL SHARP.

IN 1922, the Director of the Wellcome Bureau of Scientific Research received from Colonel Kennedy, I.M.S. (retd.), a series of small specimens of drugs collected near and used in the Yerpa Monastery in Lhasa. The only specimen of more than anthropological interest was an aconite root, which was identified by Dr. Stapf of the Royal Botanic Gardens, Kew, as *Aconitum rotundifolium*, Kar. and Kir. As this rare species of aconite has not been examined chemically, Colonel Kennedy was kind enough to obtain a further supply of leaves (360 g.) and roots (1,250 g.), collected on the pass between Sikkim and the Chumbi Valley in Tibet at an altitude of about 12,000 feet. This material we now have good reason to believe is not *A. rotundifolium*, and we propose to call it for the present "Chumbi aconite." Colonel Kennedy suggested that Major F. M. Bailey, C.I.E., Political Resident in Sikkim, might be able to obtain more. Major Bailey sent out collectors on two occasions, but the material obtained, on examination by Dr. Stapf, proved to be of the *A. spicatum* type, and as the authors subsequently found that it contained pseudaconitine, instead of the bikhaconitine characteristic of *A. spicatum*, Dr. Stapf agrees that it may be *A. Balfourii*, Stapf.

The latter on examination at the Imperial Institute (*Bull. Imp Inst.*, 1906, **4**, 38) was found to contain pseudaconitine, but nc detailed evidence for this has been published. The authors are greatly obliged to the authorities of the Imperial Institute for providing them with specimens of the roots then examined and o: the alkaloid obtained. The results of this comparison leave nc doubt that the alkaloid of *A. Balfourii* is pseudaconitine.

The opportunity has been taken to characterise pseudaconitin more completely and to make a preliminary examination of it oxidation products. For these purposes a considerable quantity o the alkaloid has been prepared from the usual source, *A. deinorrhizum* Stapf (*A. ferox* var. *atrox*, Wall.). Among the new salts prepared ar the *hydrochloride*, which had not hitherto been obtained crystalline and the *picrate*, which, unlike the picrates of most of the aconitines crystallises easily. The formula generally accepted for pseud aconitine is $C_{36}H_{49}O_{12}N$. Neither the authors' combustion result nor those on which Wright and Luff (J., 1878, **33**, 151), Dunstar and Carr (P., 1895, **11**, 154; J., 1897, **71**, 350), Freund and Nieder hofheim (*Ber.*, 1896, **29**, 852), and Schmidt (*Arch. Pharm.*, 1909 **247**, 240) based this formula are in particularly good agreement with the figures calculated from it. Dunstan and Andrews (J. 1905, **87**, 1636) altered the formula to $C_{36}H_{51}O_{12}N$, which the authors propose to adopt, at least provisionally.

It is common ground with previous investigators that pseud-aconitine on hydrolysis furnishes pseudaconine, $C_{25}H_{41}O_8N$, and one molecular proportion each of acetic and veratric acids, and that it contains six methoxyl groups (Freund and Niederhofheim, *loc. cit.*). In the present paper, it is shown that the two remaining oxygen atoms function as hydroxyl groups, since pseudaconine yields a well-crystallised tetra-acetyl derivative, and that the nitrogen is present as a methylimino-group.

Carr has stated that on oxidation with permanganate pseud-aconitine yields acetaldehyde and a crystalline substance, m. p. 235° (J., 1912, **101**, 2243). We are able to confirm the formation of acetaldehyde, but the solid oxidation product is a complex mixture, which so far we have not been able to separate satisfactorily into its components.

On oxidation with chromic acid, pseudaconitine yields a crystalline *substance*, $C_{34}H_{45}O_{11}N$, which contains one methoxyl group less than its progenitor, but retains intact the methylimino-group. It is neutral in reaction, but can be induced to form salts which are hydrolysed by water. The weakly basic character of this substance as compared with pseudaconitine may be due to the formation of a carbonyl group next to the nitrogen, by the oxidation of a secondary

alcohol group, in a manner similar to that taking place in the oxidation by nitric acid (see below). On hydrolysis by alkalis, the substance yields acetic and veratric acids and a crystalline product, which should be represented by the formula $C_{23}H_{35}O_7N$, but which so far we have not been able to confirm by analysis.

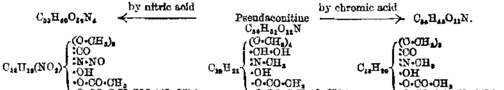
On oxidation with cold nitric acid pseudaconitine yields two products, a pale yellow, crystalline *substance A*, having the formula $C_{33}H_{40}O_{16}N_4$, and a bright yellow *substance B*, $C_{34}H_{43}O_{17}N_3$. Product A still contains the acetyl group, but the veratroyl residue has been nitrated in position 6; the number of methoxyl groups has been reduced to five, two of which belong to the nitroveratroyl radical, so that one has disappeared from the nucleus; the methylimino-group has been converted into a :N·NO group, since the compound gives Liebermann's nitrosoamine reaction; and the remaining nitrogen is probably present as a nitro-group, indicating the presence of a benzene ring in the nucleus. Of the two remaining oxygen atoms, one is present as a hydroxyl group. Evidence for this and simultaneous confirmation of the presence of a :N·NO group was obtained in the following way. The oxidation product A was treated with acetyl chloride at 100° under pressure. The excess of reagent was distilled off, carrying with it nitrosyl chloride formed hy the conversion of the :N·NO group into a *N*-acetyl group. The acetylated material contained two substances, of which one was obtained crystalline. This no longer gave the nitrosoamine reaction and on hydrolysis furnished three molecular proportions of acetic acid, *two* by alkaline hydrolysis and *one* by subsequent acid hydrolysis. The first two are formed (*a*) from the acetyl group originally present in pseudaconitine and persisting in A and (*b*) from an acetyl group formed in this reaction by acetylation of a hydroxyl group in A. The third molecule of acetic acid comes from the acetyl group attached to nitrogen hy replacement of the nitroso-group in this reaction.

This still leaves one oxygen atom in A to be accounted for. Its function is shown by the behaviour of the crystalline *substance*, $C_{22}H_{31}O_{10}N_3$, formed along with acetic and 6-nitroveratric acids by the alkaline hydrolysis of A. On solution in methyl alcohol containing sodium methoxide, it is converted into a crystalline *sodium* salt, $C_{22}H_{32}O_{11}N_3Na$, produced by addition of the elements of a molecule of sodium hydroxide, which clearly implies the presence of a lactim group in this hydrolytic product and also in A. This indicates that in pseudaconitine there is present a group such as ·NMe·CH·OH, which is converted by treatment with nitric acid into the structure ·N(NO)·CO·, and this on treatment with alkali passes into ·NH(NO)⁝CO·ONa. That a considerable change in the

state of combination of the nitrogen takes place in this last reaction is clear from the fact that, whereas pseudaconitine, A, and the hydrolytic product of the latter all fail on distillation to yield vapours giving the pyrrole pine-shaving test, this test is readily given by the vapours from the sodium salt, and from the ill-defined materials formed by the action of hydrochloric acid, thionyl chloride, and various oxidising and reducing agents on the hydrolytic product. The production of volatile pyrrole derivatives in this fashion does not of necessity imply the presence of a pyrrole nucleus in pseudaconitine or its proximate degradation products now described, but merely that in the hydrolytic product of A the nucleus is in such a form as to yield pyrrole derivatives readily in the somewhat drastic process of dry distillation.

The examination of the bright yellow nitric acid oxidation product B has not been carried very far. On hydrolysis it furnishes acetic and 6-nitroveratric acids and an amorphous nitrogenous product: it contains five methoxyl groups, of which two are in the nitroveratroyl residue, and a nitroso-group which is eliminated on treatment with acetyl chloride as in the case of product A, but neither in this nor in any of the numerous reactions tried on this substance has any well-defined crystalline product been obtained.

In the formation of the chromic acid oxidation product, $C_{34}H_{45}O_{11}N$, and of the nitric acid oxidation product A, $C_{33}H_{40}O_{16}N_4$, very little effect has been produced on the nuclear structure of pseudaconitine, as will be seen from the following tabular summary of what is known regarding the three substances :



The products obtained, moreover, are not promising for gradua further degradation owing to their tendency to produce solubl colloidal substances, and other methods of dealing with the problen are now being investigated.

Most of the substances described in this paper have prove difficult to analyse by combustion, but the hydrolytic products o the chromic acid oxidation product and of the substance A wer particularly troublesome in this respect, and we have been fortunat in having the analyses on which we have based the formula $C_{22}H_{31}O_{10}N_3$, confirmed by Professor R. Robinson, who had micro analyses made in his laboratory by Mr. A. Bennett, for which w take this opportunity of expressing our thanks.

Considerable difficulty has also been experienced in getting atisfactory determinations of nitrogen in pseudaconitine and its egradation products, due, no doubt, to the ease with which these ubstances evolve methane (Dunstan and Carr, P., 1896, **12**, 48). 'his difficulty has probably been encountered by other workers, s no determination of nitrogen in pseudaconitine appears to have een recorded since that due to Wright and Luff (*loc. cit.*). This ifficulty has been overcome by using a coil of oxidised copper eyond the reduced copper spiral of the ordinary Dumas method, as ecommended by Pregl in his micro-analytical method.

Examination of the alkaloid from the "Chumbi aconite" collected y Colonel Kennedy indicates that it is one of the possible acetyl-enzoylaconines, of which the two best known are aconitine from 1. *Napellus* and japaconitine, obtainable from various species of conite found in Japan. Most of the recent work on these two lkaloids indicates that they are not identical, but isomeric. The ifference between them may depend on the relative positions of the wo acyl groups, since they both appear to yield the same aconine, ut as they also both furnish, on oxidation by permanganate, the ame oxonitine, in which the two acyl groups are still present, they nay be merely stereoisomeric. Aconine must contain five hydroxyl roups, since aconitine yields a triacetyl derivative (Dunstan and Carr, J., 1895, **67**, 462), and this, by the replacement of two hydroxyls at a time by two acyloxy-radicals, admits of the existence of a large umber of isomerides, which may differ but little in properties. In wo recent papers, Majima and his colleagues (*Ber.*, 1924, **57**, 1466) ave shown that aconitine (Merck) consists of two isomerides A and B and from seven species of *Aconitum* found in Japan six isomerides ave been isolated (*ibid.*, p. 1456), none of the species yielding less han two and most of them four. Japaconitine (Merck), according o these authors, is a mixture of four of these isomerides. The evidence so far brought forward is scarcely sufficient to justify the view that these eight acetylbenzoylaconines are all different, but theoretically there is no reason to doubt their existence. The someride now found in the "Chumbi aconite" on the whole esembles aconitine rather than japaconitine (Dunstan and Read, J., 1900, **77**, 45), but this may be due to the fact that, although much work has been done on aconitine, it is not yet a well-characterised alkaloid. Until a further supply of the roots can be obtained the exact relationship of this alkaloid to the other acetylbenzoyl-aconines cannot be finally established. It is of interest to note that in Stapf's classification of Indian aconites *A. rotundifolium* is placed with the non-poisonous "anthora" group. The "Chumbi aconite" collected by Colonel Kennedy cannot therefore be derived from

A. rotundifolium and cannot be identical with the material originally obtained by Colonel Kennedy at the Yerpa Monastery. Dr. Stapf is of the opinion that the "Chumbi aconite" is allied to *A. spicatum*, but it cannot be definitely identified until more complete botanical material is available. It is of special interest since it is the first recorded instance of an acetylbenzoylaconine being found in an Indian aconite, for although various Indian species have at different times been confused with *A. Napellus*, it seems to be well established now that the latter species has not been found in India.

Dr. Stapf places *A. Balfourii* with *A. deinorrhizum* and, as is now shown, both these species contain the same alkaloid, pseudaconitine.

We should like to take this opportunity of thanking Colonel Kennedy for his kindness in placing his material at our disposal, Dr. Stapf for his unfailing help in identifying botanical material, and Colonel Gage, late Director of the Botanical Survey of India, Major Bailey, Political Resident in Sikkim, and Mr. W. J. Lambert, Conservator of Forests, Jammu and Kashmir State, for their kind assistance in the collection of material.

EXPERIMENTAL.

Aconitum Balfourii *and* A. deinorrhizum.

Extraction of Alkaloids.—The finely ground, air-dry roots were percolated to exhaustion with cold 95% alcohol, the percolate concentrated to low bulk under reduced pressure, and the alkaloids extracted from the residue with 0·5% hydrochloric acid. The acid solution (*A*), after agitation with ether to remove traces of acids resin, and oil, was made alkaline with sodium carbonate solution and extracted with ether, so long as this continued to remove alkaloid and after that with chloroform, which took out all but traces. On the removal of the solvent from the ethereal solution pseudaconitine crystallised out. The *A. Balfourii* roots yielded 1·2% of total alkaloid, of which 0·4%, expressed on the air-dry roots, was crystalline. This procedure was modified in working up larger quantities of *A. deinorrhizum* roots. Here the dilute hydrochloric acid extract (*A*) was filtered and the alkaloidal hydrochlorides were extracted by long-continued agitation with chloroform. The chloroform extract was dried over anhydrous sodium sulphate, and an aqueous solution of the residue left after removal of the chloroform was treated with charcoal and filtered into a 50% excess of sodium carbonate solution with constant stirring. The precipitated alkaloids (yield, 0·9% expressed on the air-dry roots) were then collected, washed with water, and dried in a vacuum. From this dry precipitate, crude pseudaconitine was obtained by boiling it with twice its weight of 95% alcohol and filtering the hot solution;

the alkaloid then crystallised on cooling. The yield was 0·4% expressed on the air-dry roots. The acid liquor (*A*) and the sodium carbonate precipitation liquors still contained some alkaloid, which was recovered in the usual way and added to the residues left from the crystallisation of the crude pseudaconitine. The nature of the alkaloids in these residues is being investigated.

Pseudaconitine and Salts.—In the following description the melting points are corrected and, unless otherwise stated, are also decomposition points. The melting points and specific rotations recorded for salts refer to the salt dried to constant weight. The crude alkaloid was recrystallised from hot 95% alcohol until of constant melting point, 212—213°. It was further purified through the hydrobromide, and the base regenerated from the pure salt had m. p. 214°, $[\alpha]_D^{20^\circ}$ + 17·06° (in alcohol; c = 1·18) and + 22·75° (in chloroform; c = 4·76). The recorded m. p.'s for pseudaconitine vary from 201° (D. and C.) to 212° (F. and N.): for $[\alpha]_D$ Dunstan and Carr found + 18·6° (c = 1·12, in alcohol) (Found: C, 62·4, 62·7, 62·8; H, 7·8, 7·9, 7·95; N. 2·2; MeO, 27·2; NMe, 2·7. $C_{36}H_{51}O_{12}N$ requires C, 62·7; H, 7·5; N, 2·0; 6MeO, 27·0; NMe, 4·2%).

The following salts are already known and were prepared for identification of the alkaloid from *A. Balfourii*.

The hydrobromide separates from alcohol in rosettes of triangular prisms, m. p. 199°, $[\alpha]_D^{20^\circ}$ − 18·5° (in water; c = 2·56) (Found for air-dry salt: loss at 100° in a vacuum, 6·6. $C_{36}H_{51}O_{12}N,HBr,3H_2O$ requires H_2O, 6·6%. Found in dry salt: Br, 10·25. Calc.: Br, 10·4%). The nitrate crystallises from dry alcohol in triangular prisms, m. p. 198°, $[\alpha]_D^{18^\circ}$ − 17·95° (in water; c = 3·9) (Found for air-dry salt: loss at 100° in a vacuum, 1·9. Calc. for $C_{36}H_{51}O_{12}N,HNO_3,H_2O$: H_2O, 2·3%. Found for dry salt: C, 56·9; H, 6·7; MeO, 24·75; NMe, 3·4. Calc. for $C_{36}H_{51}O_{12}N,HNO_3$: C, 57·4; H, 7·0; 6MeO, 24·75; NMe, 3·9%).

The hydriodide separates from hot dilute alcohol in truncated prisms, m. p. 230° (Found for air-dry salt: loss at 100° in a vacuum, 2·5. Calc. for $C_{36}H_{51}O_{12}N,HI,H_2O$: H_2O, 2·2%).

The chloroaurate had m. p. 233°.

The data recorded above for these four salts agree as well as can be expected with those recorded by previous investigators: it is well known that the melting points of the "aconitines" and their salts vary with the rate of heating and the small discrepancies in both directions now found are no doubt due to this cause. Differences in the amounts of water of crystallisation found in the hydrobromide (3 instead of $2H_2O$) and nitrate (1 instead of $3H_2O$) from those recorded by Dunstan and Carr (*loc. cit.*) are due to the

fact that these salts are efflorescent and the amount of water four depends on the conditions under which they are rendered "air-dry

The following salts are new. The *hydrochloride* was prepared l neutralising the pure base, dissolved in dry alcohol, with hydr chloric acid. The solution was then evaporated to dryness und reduced pressure, the residue dissolved in dry alcohol, and eth added; the salt then separated in twinned triangular prisms a was recrystallised from dry alcohol. It melts at 179—182° and h $[\alpha]_D^{20°} - 18{\cdot}1°$ (in water; $c = 3{\cdot}37$). When the crystals a allowed to dry in air for a short time, they appear to contain molecules of water (Found: loss in a vacuum at 120°, 10· $C_{36}H_{51}O_{12}N,HCl,4H_2O$ requires H_2O, 9·0%), but on longer exposu to air efflorescence occurs and the product is represented by t formula $C_{36}H_{51}O_{12}N,HCl,3H_2O$ (Found: loss at 120° in a vacuu 7·2. Calc.: 6·9%. Found for dry salt: C, 59·05; H, 7·2; (5·1. Calc. for $C_{36}H_{51}O_{12}N,HCl$: C, 59·5; H, 7·2; Cl, 4·9% The hydrochloride is very soluble in water and in wet alcohol ar this no doubt accounts for the failure of previous workers to obtain i

The *oxalate*, similarly prepared, crystallises from hot, dry alcoh in minute, transparent, facetted cubes, m. p. 216°. The *perchlorat* obtained as a crystalline precipitate on addition of sodium pe chlorate to a solution of pseudaconitine hydrochloride in wate crystallises from dilute alcohol in needles, m. p. 239° (Found: (54·5; H, 7·2. $C_{36}H_{51}O_{12}N,HClO_4$ *requires* C, 54·7; H, 6·6% The *picrate* crystallises from alcohol in spheroidal masses of thi orange-yellow prisms, m. p. 196°.

Pseudaconine.—A quantity of pseudaconine was prepared b hydrolysis of the residues left from the initial crystallisation pseudaconitine (p. 1110).

It is obtained from acetone in well-defined, large, colourless prism containing 1 mol. of solvent, m. p. 93—94°, $[\alpha]_D^{20°} + 38{\cdot}7°$ (in water $c = 1{\cdot}69$) (Found in air-dried substance: C, 62·1; H, 8·8; loss a 120° in a vacuum, 10·4%. Calc. for $C_{25}H_{41}O_8N,C_3H_6O$: C, 62·1 H, 8·75; C_3H_6O, 10·7%). *Dunstan and Andrews* (*J.*, 1905, 87 1629) give m. p. 86—87° (after crystallisation from acetone), $[\alpha]_D$ = + 39·0° ($c = 1{\cdot}8$ in water). A *tetra-acetyl* derivative was obtaine by heating solvent-free pseudaconine (1 g.) under reflux with acety chloride (2 c.c.) for an hour. The acetyl chloride was remove by distillation and the residue dissolved in water and made alkalin with sodium carbonate; the white precipitate thus formed crystallise from ligroin in colourless, stout needles, m. p. 228°, $[\alpha]_D^{20°} - 8{\cdot}1$ (in alcohol; $c = 0{\cdot}956$) (Found in substance dried at 120° in vacuum: C, 60·5; H, 7·6; MeO, 19·35; NMe, 4·1. $C_{33}H_{49}O_{12}N$ requires C, 60·8; H, 7·6; 4MeO, 19·05; NMe, 4·5%). The acety

groups were estimated by hydrolysis with alcoholic potassium hydroxide, followed by acidification, steam distillation, and titration of the distillate (Found: acetic acid, 37·7. Calc. for four acetyl groups, 36·85%). Pseudaconine was recovered from the steam distillation mother-liquor by extraction with ether after addition of sodium carbonate in excess, the yield of pure crystalline base being 88% of that theoretically possible. The acetyl derivative, although alkaline to litmus, does not form salts and may be crystallised unchanged from solutions in alcoholic sulphuric or oxalic acid. Tetra-acetylpseudaconine causes no tingling sensation when applied to the lips. According to Dr. Trevan, Pharmacologist to the Wellcome Physiological Research Laboratories, it is not toxic to mice on subcutaneous injection in doses of 5 mg.

Oxidation of Pseudaconitine.

(1) *With Nitric Acid.*—Pseudaconitine (5 g.), treated with 30 c.c. of nitric acid (*d* 1·42) at room temperature, slowly dissolved with evolution of brown fumes and rise of temperature to about 45°. After 6 hours the clear solution was poured into water (300 c.c.); the white precipitate, which soon turned yellow, was filtered off, washed with water, and dried over-night in a vacuous desiccator; yield, 4·8 g. The aqueous filtrate, after being nearly neutralised with sodium carbonate, yielded on extraction with chloroform a further 0·5 g. This product was boiled with alcohol, which separated it into a sparingly soluble, *pale yellow substance* (*A*) and a readily soluble, *bright yellow solid* (*B*).

Oxidation product A. This substance is insoluble in water and most organic solvents, and sparingly soluble in hot acetic acid or acetone. From the latter it separates in faintly yellow prisms, which blacken at about 260° and decompose sharply at 270° (Found: C, 52·7, 52·8; H, 5·3, 5·3; N, 7·4, 7·5; MeO, 19·9, 20·6; NMe, 0. $C_{33}H_{40}O_{16}N_4$ requires C, 52·9; H, 5·4; N, 7·5; 5MeO, 20·7%). Acetic acid was estimated by the method described for tetra-acetyl pseudaconine (above) (Found: acetic acid, 8·0, 8·8. Calc. for 1 mol. produced on hydrolysis, 8·0%). A quantitative reduction with titanous chloride was carried out as follows: a solution of a weighed quantity of the substance in concentrated sulphuric acid was set aside for 3 hours, poured into water, and diluted to a definite volume. Aliquot parts of this solution were treated with excess of standard titanous chloride and boiled for 15 minutes in a current of carbon dioxide in a flask fitted with a Bunsen valve. After cooling, the excess of titanous chloride was titrated with standard iron alum solution, potassium thiocyanate being used as indicator. In this way, 16·54 and 16·61 mols. of titanous chloride were used. In view

of the large undetermined part of the molecule, these results are not regarded as conclusive, but they possibly indicate the presence in the molecule of one nitroso- and two nitro-groups (calc., 16 mols. $TiCl_3$). Further, the substance gives Liebermann's nitrosoamine reaction, and evidence is adduced later of the elimination of a nitroso-group when the substance is acetylated. Proof of the presence of one nitro-group is furnished later, in the production of 6-nitroveratric acid on hydrolysis, and the third nitrogen can hardly be in any other condition than that of a nitro-group.

Acetylation. The substance A is unaltered by boiling with acetic anhydride. On heating A (8 g.) with acetyl chloride (32 c.c.) in a sealed tube at 100° for 1 hour, an orange-coloured liquid was obtained. The excess of acetyl chloride was removed by distillation, leaving a white solid, which was twice evaporated to dryness with dry alcohol (yield, 8·45 g.). The acetyl chloride distillate was orange in colour and was fractionally distilled, practically all the colour passing over in the first few c.c. On addition of water to these first runnings the colour disappeared and the liquid gave all the usual reactions for nitrous acid. The colour is therefore evidently due to the presence of nitrosyl chloride formed by the action of acetyl chloride on a nitrosoamine group in A. The white solid is a mixture of at least two substances, one of which can be obtained in well-defined, small prisms by taking advantage of the fact that it is less soluble in boiling *iso*propyl alcohol than the remaining reaction products. For example, the crude material was boiled with *iso*propyl alcohol (100 c.c.), and the solution filtered hot from the undissolved part; the latter was again boiled with the solvent (25 c.c.), the solution was filtered hot, and the residue was dissolved in a large volume of *iso*propyl alcohol, placed on a large boiling water-bath, and left to cool slowly. Crystallisation in this fashion was repeated until the *acetyl* derivative (4 g.) had a constant melting point of 227—230°. The remaining product of the reaction has not been obtained crystalline. The crystalline product does not give Liebermann's nitrosoamine reaction, so the original nitroso-group has been replaced by an acetyl group, since nitrosyl chloride is formed in the reaction and acetic acid is produced on acid hydrolysis (see below) (Found: C, 55·3, 54·9; H, 6·1, 6·15; N, 5·4; MeO, 19·25. $C_{37}H_{45}O_{17}N_3$ requires C, 55·3; H, 5·65; N, 5·2; 5MeO, 19·3%). Hydrolysed by alcoholic potassium hydroxide in the manner described for tetra-acetylpseudaconine (p. 1113), it furnished two molecules of acetic acid (Found: acetic acid, 16·7. Calc. for two *O*-acetyl groups, 14·95%). The residue from the steam distillation gave 6-nitroveratric acid on extraction with ether. The

mother-liquors were neutralised, and evaporated to dryness under reduced pressure, and the residue was boiled with absolute alcohol, which dissolved the third product of the reaction. Numerous attempts to obtain this new substance in a crystalline condition failed, and in order to prove the presence of an *N*-acetyl group, already suggested by the formation of nitrosyl chloride, the crude material was boiled under reflux for 6 hours with 1% hydrochloric acid and steam-distilled, and the silver salt of the volatile acid was prepared in the usual fashion and shown to be silver acetate (Found: Ag, 64·5. Calc., 64·7%). The high figure found for acetic acid in the alkaline hydrolysis is no doubt due to partial hydrolysis of the *N*-acetyl group during the steam distillation of the acid liquor.

Hydrolysis of A. The oxidation product A (3·5 g.) slowly dissolved when mixed with alcohol (70 c.c.) and potassium hydroxide (1·75 g.), dissolved in a little water. After 2 hours the solution was diluted with water (3 vols.), neutralised with sulphuric acid, and filtered from a little potassium sulphate, and the alcohol was removed under reduced pressure on a water-bath. After cooling, the solution was made acid with sulphuric acid and steam-distilled, the steam-distillate was neutralised with sodium hydroxide and evaporated to dryness, and a solution of the residue in a little water was filtered and treated with silver nitrate. The precipitated silver salt was dried over sulphuric acid in a vacuous desiccator (Found: Ag, 64·3. Calc. for silver acetate: Ag, 64·7%). From the liquor left after steam distillation, ether extracted a yellow acid, m. p. 195° after crystallisation from water (Found: C, 47·2; H, 4·4. Calc. for 6-nitroveratric acid, $C_9H_9O_6N$: C, 47·55; H, 4·0%) and also when mixed with 6-nitroveratric acid (m. p. 194°). Further, the methyl ester of the acid from A, alone or mixed with methyl 6-nitroveratrate, melted at 143·5° (Found for the methyl ester: C, 49·3; H, 4·8. Calc.: C, 49·8; H, 4·6%). The mother-liquors from the ether extraction, on repeated agitation with chloroform, yielded 1·25 g. of a colourless solid. If the liquor has become concentrated during the steam distillation, some of this solid is precipitated on shaking with chloroform. This *hydrolytic product of A* crystallises well from alcohol, benzene, or chloroform in colourless, shining needles containing an indefinite amount of solvent. On heating, it froths at 85—115°, the actual temperature depending on the solvent used, but in no case sharply. If crystallised from water and air-dried, it melts with frothing at 165—170°. When quite dry, it has m. p. 215°, and $[\alpha]_D^{20°}$ + 30·9° ($c = 0·59$, in alcohol). For analysis the substance was dried first at 80° and finally at 140° in a vacuum

(Found: C, 53·2, 53·1, 52·74*; H, 6·2, 6·3, 6·11*; N, 8·34*, 8·32*, 8·3; MeO, 18·9; *M*, cryoscopic in nitrobenzene, 487. $C_{22}H_{31}O_{10}N_3$ requires C, 53·1; H, 6·3; N, 8·45; 3MeO, 18·7%; *M*, 497·3).

Action of sodium methoxide. On treating the substance $C_{22}H_{31}O_{10}N_3$ (1 g.) with excess of a 12% solution of sodium methoxide in methyl alcohol (1·3 c.c.) a syrup formed. This practically all dissolved when stirred with methyl alcohol (10 c.c.), and after a few minutes needle-shaped crystals of the *sodium* salt began to separate; these were collected after 12 hours, washed with a little alcohol, and dried in a vacuous desiccator (0·94 g.) (Found: Na, 4·1. $C_{22}H_{32}O_{11}N_3Na$ requires Na, 4·3%). The salt was unaltered in composition after being boiled with acetone, in which it is sparingly soluble. On heating, the substance gives the pyrrole pine-shaving test. It is very soluble in water, forming a faintly alkaline liquid which does not give precipitates with salts of the heavy metals.

Reduction with titanous chloride. The hydrolytic product of A was reduced in the manner described for the oxidation product itself (p. 1113), but the preliminary treatment with sulphuric acid was omitted, as the compound is soluble in water. It required 10·89, 10·90 mols. of titanous chloride for reduction, indicating the probable presence of a nitro- and a nitroso-group (calc., 10 mols.).

Action of acetylating agents. When the hydrolytic product of A is treated with acetyl chloride in a sealed tube at 100° a white solid is formed which has so far not been crystallised. When boiled with acetic anhydride, it furnishes a well-defined *substance* crystallising from alcohol in prismatic needles, m. p. 257° (decomp.), togethe with a small amount of a second crystalline compound, decomp. 322° The main product, which retains the nitrosoamino-group, give analytical figures (except for methoxyl) agreeing with those calculate for a diacetyl derivative. The change is, however, probably mor deep-seated, since the original substance is not regenerated when th compound is hydrolysed (Found: C, 53·4, 53·4; H, 6·25, 6·3 ot gJ, 7·5; MeO, 18·9. $C_{26}H_{35}O_{12}N_3$ requires C, 53·7; H, 6·1; N, 7·2 roup hO. 16·0%). We hope to return to the study of this interestin formed in se when more material is available.

see below) (hydrolytic product of A does not react with semicarbazid 9·25. $C_{37}H_{45}$ ethyl iodide under a variety of conditions. Reductio 9·3%). Hydrol with hydriodic acid, titanous chloride, and sodium an nanner described:

wo molecules of abted to Mr. A. Bennett for these results obtained by Pregl wo *O*-acetyl group ethod. Great difficulty was experienced in getting sati ation gave 6-nitro results for this substance and the other figures recorded a 20 combustion figures, about half of which were in go formula.

alcohol did not yield any product which could be characterised. Oxidation with permanganate and with chromic acid gave very soluble substances, which could not be purified. On boiling with concentrated hydrochloric acid an amorphous substance was obtained which formed organogels. Attempts to purify this substance by means of a Berkefeld filter did not lead to any conclusive results; it still contains a methoxyl group, but also contains chlorine, and gives the pyrrole pine-shaving reaction. Treatment in a sealed tube with hydrochloric acid at 170° gave rise to methyl chloride, ammonium chloride, and a black, humus-like acidic substance.

The product of the action of phosphorus trichloride on the hydrolytic product gives the pyrrole pine-shaving test; it yields, on solution in dilute sodium hydroxide and extraction with ether, a small amount of an oily substance, which smells strongly of indole, but does not give colour reactions with Nelson's or Ehrlich's reagent. Extraction with chloroform gives a similar small quantity of an oil with an indole-like but rather sweeter smell. No other product was isolated.

Oxidation product B. The orange-coloured substance B (p. 1113) has not been obtained definitely crystalline. It may be purified by extraction in a Soxhlet apparatus with dry ether, in which it is sparingly soluble, and is thus slowly deposited in the flask as a bright yellow, granular powder, which slowly decomposes at 195° but does not melt. After purification in this way it separates from alcoholic solutions in a granular condition with the decomposition point unchanged (Found: C, 53·35, 53·5; H, 5·6, 5·8; N, 5·2, 5·6; MeO, 20·0, 20·2; MeN, 0; *M*, in camphor by Rast's method, 774. $_4H_{43}O_{17}N_3$ requires C, 53·3; H, 5·7; N, 5·5; 5MeO, 20·3%; , 765·4). It contains a nitrosoamino-group which, like that of :idation product A, is removed on treatment with acetyl chloride; ıt no definite acetyl derivative could be obtained. On hydrolysis r alcoholic potash, B yields one molecule each of acetic and nitroveratric acids, which were identified as described already ·. 1115). The other product of hydrolysis is an intractable, amorıous, orange-coloured substance.

(2) *Oxidation with Chromic Acid.*—When a solution of pseud-:onitine (5 g.) in 10% sulphuric acid (30 c.c.) was treated with ›tassium dichromate (3·4 g.) in water (145 c.c.) an orange-coloured, 'anular precipitate was obtained which dissolved after 3 hours' heat-g on a water-bath. After cooling, the solution was extracted with ıloroform, which removed a dark-coloured substance (4·5 g.) contain-g chromium. This solid was extracted with 0·5% sulphuric acid ıd the part undissolved (2·47 g.) was crystallised from alcohol. The

oxidation product was thus obtained in colourless, irregular prisms (2·05 g.), decomp. 255°, $[\alpha]_D^{20°} + 67·95°$ (Found: C, 63·4, 63·6, 63·3; H, 7·1, 7·0, 7·2; N, 2·1; MeO, 24·3, 23·6; NMe, 3·4. $C_{34}H_{45}O_{11}N$ requires C, 63·4; H, 7·05; N, 2·2; 5MeO, 24·1; NMe, 4·5%). The substance is insoluble in water, its solution in dilute alcohol is neutral, but it forms salts in presence of excess of acids. The *hydrochloride* was prepared by dissolving the substance in a considerable excess of 10% hydrochloric acid, evaporating the solution to dryness under reduced pressure, and crystallising the dried salt from a mixture of dry alcohol and dry ether: it was thus obtained in stout, glistening needles, which when quite dry frothed at about 180°; $[\alpha]_D^{20°} + 39·5°$ (in dry alcohol; $c = 1·006$) (Found C, 60·1; H, 6·9; Cl, 5·2. $C_{34}H_{45}O_{11}N,HCl$ requires C, 60·0; H 6·8; Cl, 5·2%). The salt is soluble in cold water, but rapidly dissociates on warming. The *picrate*, prepared in the usual way from the hydrochloride, crystallised from dry acetone, on addition of dry ether, in balls of stout, short, yellow needles, m. p. 229—230 (Found: C, 55·15; H, 5·5. $C_{34}H_{45}O_{11}N,C_6H_3O_7N_3$ require C, 55·0; H, 5·55%). The *chloroaurate* separates from dry alcoho as a granular, yellow powder which sinters at 175°, decomposes a 185°, and is of anomalous composition (Found: Au, 16·2 $4C_{34}H_{45}O_{11}N,3HAuCl_4$ requires Au, 16·5%).

Hydrolysis. The oxidation product (5 g.) was mixed with alcoho (100 c.c.) and 50% potassium hydroxide solution (10 g.) and left t stand for 24 hours; water (100 c.c.) was then added, and the undis solved solid (1·75 g. of unchanged material) filtered off. The filtrat was neutralised with sulphuric acid and filtered from potassiur sulphate, and the alcohol removed by distillation. After coolin the solution was acidified with sulphuric acid and the precipitat formed was collected (0·48 g.). The filtrate was extracted wit benzene, the benzene extract added to the precipitate, and the who dissolved in hot water, from which veratric acid crystallised i colourless needles, m. p. 187°; it was identified by a mixed meltin point determination. The original filtrate was steam-distilled, ar acetic acid identified in the distillate by preparation and analys of the silver salt (Found: Ag, 63·9. Calc.: Ag, 64·7%). Th steam-distillation residue was made alkaline with sodium carbona and extracted with chloroform, yielding a reddish varnish (1·65 g which, when dissolved in dry alcohol and treated with dry ethe crystallised as balls of fine, faintly pink needles, m. p. 175—177 This substance should have the composition $C_{23}H_{35}O_7N$, but has proved difficult to get consistent results with it on analysis a the material clearly needs further investigation.

"*Chumbi Aconite.*"

The total alkaloid was extracted separately from the roots and leaves by the process described for *A. Balfourii* (p. 1110). The roots yielded 1·1%, and the leaves 0·2%, of total alkaloid, of which one-half and one-quarter, respectively, were obtained as crude crystalline alkaloid melting at 197°. This was converted successively into the hydrobromide, hydriodide, and hydrochloride, each of these salts being recrystallised until of constant melting point. Finally, the pure base (3 g.) was regenerated from the hydrochloride and crystallised from alcohol; it then formed thin, hexagonal plates, m. p. 203° (corr.; decomp.), $[\alpha]_D^{20^\circ}$ + 16·3° (in chloroform; c = 3·84). It was carefully compared with (1) Dunstan and Read's japaconitine, of which a small specimen was kindly provided by the authorities of the Imperial Institute, and (2) a specimen of carefully purified aconitine made from *A. Napellus* grown in England. The melting points of the three alkaloids taken simultaneously were 203°, 203°, 204°, respectively. Mixtures of the first two showed no depression, and either of the first two mixed with the third depressed the melting point of the latter, but only to 203°. The melting point of aconitine from *A. Napellus* is generally stated to be 197—198°, but this refers in nearly all cases to Merck's aconitine, which, according to Majima and his colleagues (*loc. cit.*), consists mainly of an alkaloid (aconitine-A), m. p. 202—203°, $[\alpha]_D^{14^\circ}$ + 18·1° in chloroform. The only other difference noted between the alkaloid of "Chumbi aconite" and that of *A. Napellus* was that the former appeared to be more soluble in ether. On analysis the two alkaloids, after drying at 110° in a vacuum, gave the following results:

"Chumbi aconite" (1) base: C, 62·6, 62·5; H, 7·6, 7·5; N, 2·2%.
(2) hydrobromide: C, 55·6; H, 7·0; Br, 10·5, 10·8%.

A. Napellus (1) base: C, 63·1; H, 7·4%.
(2) hydrobromide: C, 56·0; H, 7·1; Br, 11·6%.

Calc. for $C_{34}H_{47}O_{11}N$: C, 63·2; H, 7·3. Calc. for $C_{34}H_{47}O_{11}N,HBr$: C, 56·2; H, 6·7; Br, 11·0%.

Calc. for $C_{34}H_{49}O_{11}N$: C, 63·0; H, 7·6. Calc. for $C_{34}H_{49}O_{11}N,HBr$: C, 56·0; H, 6·9; Br, 11·0%.

There is naturally little to choose between these formulæ, but the results for the alkaloid from Chumbi aconite agree better with the figures required by $C_{34}H_{49}O_{11}N$, the formula assigned by Dunstan and Read (*loc. cit.*) to japaconitine, than with $C_{34}H_{47}O_{11}N$, which is the formula accepted for aconitine from *A. Napellus* (compare Majima, *loc. cit.*).

The principal constants of the alkaloid from Chumbi aconite (C)

and its salts are given in the following table and compared with those usually accepted for aconitine (A) and japaconitine (J) and their salts. The melting points and the specific rotations given are for the anhydrous substance in each case, unless stated otherwise, and the solvents are chloroform for the bases and water for the salts. Figures shown in parentheses are new determinations made in the course of this work with the English aconitine already referred to above.

	Bases.			Hydrobromides.		
	C.	A.	J.	C.	A.	J.
M. p. ...	203°	197—198° (204°)	203°	175°	(176—180°)	172—173°
$[\alpha]_D$	+16·3°	+14·6° (+17·3°)	+20·26°	−34·8°	−30·8° (−29·1°)	—

	Hydrochlorides.			Hydriodides.		
	C.	A.	J.	C.	A.	J.
M. p.	174°	149° * (174°)	149° *	225°	226°	195°
$[\alpha]_D$	−35·9°	−35·4° (−29·2°)	−25·1°	—	—	—

* Probably hydrated salts.

It will be seen that all three alkaloids have similar constants and that the alkaloid from Chumbi aconite more closely resembles aconitine than it does japaconitine. With regard to the discrepancies between the pair it may be pointed out that, although 197—198° is usually accepted as the melting point of aconitine, the specimen of aconitine used in this instance had m. p. 204°, which is close to that (202—203°) recorded by Majima and his co-workers for the aconitine-A they isolated from Merck's aconitine (m. p. 197—198°). The melting point recorded for aconitine hydrobromide varies from 163° to 206—207°. In the authors' experience and under the conditions maintained throughout their determinations, it melts when quite dry at 176—180°; if the dry salt is left in the air for a few minutes, some sintering occurs at 160—163°, and if the temperature is then slowly raised the salt never really melts but decomposes above 200° (compare Schulze, *Arch. Pharm.*, 1906, **244**, 170). The hydrobromide of the alkaloid from Chumbi aconite behaves similarly, but differs in melting quite sharply at 175° under the standard conditions and when quite dry. In recrystallising this hydrobromide from water, a minute quantity of a sparingly soluble salt, m. p. 199° (corr.), was eliminated. It is possible that the long range of melting point usually attributed to aconitine hydrobromide is due to the salt being a mixture, and it is noteworthy that both forms of Majima's aconitine-A hydrobromide are stated to melt sharply.

The English aconitine used by the present authors gave $[\alpha]_D^{20°}$

$-29 \cdot 1°$ for the hydrobromide and $[\alpha]_D^{20°}$ $-29 \cdot 2°$ for the hydrochloride. Unfortunately Majima and his co-workers give no figures for the specific rotations of the salts of their aconitines-A and -C. The chloroaurate of the alkaloid of Chumbi aconite, crystallised from alcohol, melts at 136° (air-dry) and at 152° (dried at 100°). The corresponding melting points for aconitine chloroaurate are 136° and 151—152°.

None of the crystallised alkaloid could be spared for hydrolytic experiments, but the residual amorphous alkaloids (7·8 g.) were hydrolysed by keeping them in alcoholic potassium hydroxide for 2 days. The liquors were worked up as described on p. 1118, the bases being extracted with ether (yield, 1·2 g.) and chloroform (yield, 2·4 g.). Both residues were acetylated in the cold with acetyl chloride and yielded the same crystalline product (1 g.) which, when recrystallised from boiling alcohol, had m. p. 241°, $[\alpha]_D^{20°}$ $-32 \cdot 5°$ (in chloroform; $c = 2 \cdot 625$) (Found: acetic acid, 33·1. Calc. for four acetyl groups in $C_{33}H_{49}O_{13}N$: acetic acid, 35·9%). These figures agree with those (m. p. 241—242°, $[\alpha]_D$ $-33 \cdot 7°$) recorded by Majima, Suginomé, and Morio (*Ber.*, 1924, **57**, 1466, 1472) for the tetra-acetyl derivative of aconine-A derived from both jesaconitine (acetylanisoylaconine) and the aconitine-A isolated from Merck's aconitine. The alkaline aqueous liquid was acidified and shaken with ether, which extracted benzoic acid (m. p. 121°). The residual liquor was steam-distilled, the distillate neutralised by sodium hydroxide, and sodium estimated as the sulphate in the dry residue (Found: Na, 32·4. Calc. for $C_2H_3O_2Na$: Na, 28·0%). This high result was not unexpected, as the acetic acid obtained by the hydrolysis of amorphous residual bases of *Aconitum* species is in our experience never pure.

These observations on the amorphous bases of Chumbi aconite on the whole tend to support the view that the crystalline base of this plant is aconitine.

The authors desire to record their indebtedness for help in the course of this work to their assistants, the late Mr. S. E. Pusey, Messrs. F. Walton, L. Barnett, and H. C. Clarke, and to Dr. H. A. D. Jowett for kindly undertaking, at Messrs. Burroughs Wellcome & Co.'s works at Dartford, the preliminary extraction of the considerable quantity of *A. deinorrhizum* roots used.

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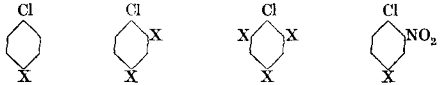
CXLII.—*The Comparative Effects of the Nitro-, Carboxyl, and Sulphonic Acid Groups on the Hydrolysis of Aryl Halides.*

By WILLIAM DAVIES and EDNA SWALLOW WOOD.

THE almost complete lack of activity of chlorine in 1 : 3-dichlorobenzene-4 : 6-disulphonic acid as compared with its great activity in 1 : 3-dichloro-4 : 6-dinitrobenzene has already been noticed (J., 1927, 1122). The effect of the nitro-group on *o*- and *p*-halogen atoms is great and well known (compare Kenner, J., 1914, **105**, 2717; Holleman and collaborators, *Rec. trav. chim.*, 1921, **40**, 67). Partly from a consideration of their activating effects on other atoms or groups in the same molecule, the carboxyl and the sulphonic acid groups, like the nitro-group, have been classified as positive (Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, ii, 2). However, the chief and almost the only experimental investigation of the activating effects of these two groups on halogen atoms in the benzene nucleus has been carried out by Schöpff and his collaborators, who deduced the following rule from their results (*Ber.*, 1891, **24**, 3784, where references to previous experimental work are given) :—" Das Halogenatom des Benzolkernes ist bei gleichzeitiger Anwesenheit zweier negativer Gruppen in o- und p- Stellung, der gleich oder ungleich sein konnen, leicht durch andere zu ersetzen; ist nur eine negative Gruppe vorhanden, so findet keine Umsetzung statt, ausser bei der Nitrogruppe." One of the results of the rule has been the adoption in preparative work of precautions against hydrolysis in compounds of the type examined by Schöpff (see p. 1126).



(I.) (II.) (III.) (IV.)

This paper records a comparison of the effects of the groups mentioned in the title on the reaction $RCl + 2KOH = ROK + KCl + H_2O$.

Martinsen (*Z. physikal. Chem.*, 1907, **59**, 605) has shown that the speeds of nitration of nitrobenzene, benzenesulphonic acid, and benzoic acid are

CO_2H $(K = 100) > SO_3H(K = 26{\cdot}0) > NO_2(K = 1{\cdot}5)$. Series A.

Since benzoic acid (19·8%), benzenesulphonic acid (10%), and nitrobenzene (about 6·5%) undergo under similar conditions ortho-para-nitration to the extents indicated in parenthesis (Holleman, " Die

direkte Einführung von Substituenten in den Benzolkern," pp. 124, 75, and 71 respectively), it is evident that no very exact quantitative meaning can be assigned to Martinsen's figures, which refer to total and not merely meta-nitration. Nevertheless Martinsen's results may be accepted as indicating in a roughly quantitative way the activation of meta-standing hydrogen.

The experiments now to be described show that the order of activation of the chlorine atom in (I), (II), (III), and (IV) produced by X (CO_2H, SO_3H or NO_2) is

$$NO_2 > SO_3H > CO_2H \quad . \quad . \quad . \quad . \quad \text{Series B.}$$

The activating powers of the three groups are, however, very different. So great is that of the nitro-group in comparison with the other two groups that only extremely rough figures can be given. In compounds of type (II) the chlorine in the nitro-compound is more than 70,000 times as reactive as that in the sulphonic acid and more than 200,000 times as reactive as that in the carboxylic acid. These figures merely represent lower limiting values as is explained on page 1131, and the nitro-compounds are in reality far more reactive than they indicate.

p-Chlorobenzenesulphinic acid also has been compared with the analogous substances (I) examined: the chlorine atom is slightly more mobile than that in *p*-chlorobenzenesulphonic acid. The experiments, however, necessitated temperatures above 100°, and it is possible that some of the sulphinic acid changed to *p*-chlorophenyl disulphoxide (compare Otto, *Annalen*, 1868, **145**, 323), which might possibly be much more reactive than the original sulphinic acid. In any event, it is clear that the sulphinic acid group confers the same order of activity as the sulphonic acid and the carboxyl group.

No doubt the unique character of the nitro-group depends on or is closely connected with the fact that aromatic nitro-compounds (compare *s*-trinitrobenzene and picric acid) readily form addition compounds (compare Kenner, *loc. cit.*; Kenner and Parkin, J., 1920, **117**, 852), whereas sulphonic and carboxylic acids have this tendency very slightly, if at all, developed. Not only does the nitro-group make a suitably placed chlorine atom reactive, but it seems to put the molecule into a reactive phase, and enables a suitably placed sulphonic or carboxylic acid group to produce an enormously greater effect than it does in the molecule without a nitro-group. For example, the activity of the chlorine in *p*-chlorobenzenesulphonic or *p*-chlorobenzoic acid is so small that it cannot be measured at ordinary pressures in a reasonable time. But in compounds of type (IV) the chlorine atom in the sulphonic acid is about 16, and that in the carboxylic acid about 4·4, times as reactive as the chlorine in

o-chloronitrobenzene (see Series II). This great increase in the effect of the weaker groups in conjunction with a nitro-group seems to show that the nitro-group may owe its unique activating power to its ability to form intermediate compounds, of which the other groups, when in the same molecule, may take advantage.

The significance of the fact that the order in Series A is the reverse of that in Series B will be dealt with in a later communication. Meanwhile it may be noted that Schöpff's rule is on the whole correct, though the relatively extraordinarily great effect of the nitro-group is not indicated. The carboxyl or sulphonic acid group alone has too small an activating power at moderate temperatures to justify such precautions to prevent hydrolysis as those referred to on p. 1126. At high temperatures, however, the weaker *activating groups show considerable effect, as, e.g., in the preparation* of diphenylamine-2 : 4 : 6-trisulphonanilide (p. 1125).

Experimental.

The Preparation and Purification of Materials.—*o*- and *p*-Chloronitrobenzenes are recrystallised from methylated spirit until they melt sharply at 32° and 83°, respectively.

Sulphonic acids. The sulphonyl chloride is boiled with methylated spirit for 2 hours and then water is gradually added at intervals to the boiling solution until the ester first formed is completely hydrolysed, as shown by no precipitation occurring on further addition of water. The solution, after being freed from hydrochloric acid by repeated evaporation nearly to dryness with suitable additions of water (it is also free from sulphate), is filtered, diluted to a convenient concentration, and standardised by titration with potassium hydroxide. The purity of the sulphonic acid is checked by an analysis of the potassium salt.

Chlorobenzene-*p*-sulphonic acid. Chlorobenzene sulphonated by Baxter and Chattaway's method (J., 1915, **107**, 1815) gives even under these mild conditions a moderate amount of the sulphone (m. p. 149°), which is easily separated from the acid. The barium salt gives a good yield of chlorobenzene-*p*-sulphonyl chloride (m. p. 53°) when heated with phosphorus pentachloride (Found in the anhydrous potassium salt: K, 16·8. Calc.: K, 16·95%).

Chlorobenzene-2 : 4-disulphonic acid. Since, owing to the tendency to sulphone formation, chlorobenzene cannot conveniently be disulphonated, phenol is disulphonated and the hydroxyl group then replaced by chlorine. This process is based on that of Pollak, v. Fiedler, and Roth (*Monatsh.*, 1918, **39**, 179), who obtained a mixture of *chlorobenzene di- and tri-sulphonyl chlorides.* It is more convenient to mono- and di-sulphonate phenol, and the corresponding

chlorobenzene-mono- and -di-sulphonyl chlorides can be separated by distillation under very low pressure. Phenol (499 g.) is heated with 96% sulphuric acid (870 c.c.) in the water-bath for 4 hours, 50 c.c. of fuming sulphuric acid (10% SO_3) are added, and the mixture is heated for 5 hours in a brine bath at 108—110° (the temperature of the sulphonating mixture is 101—103°). Under these conditions the phenol is largely disulphonated without being trisulphonated. The sulphonic acids are converted into their calcium and thence into their sodium salts, and these, when heated with phosphorus pentachloride at 140—150°, give the mixed sulphonyl chlorides of chlorobenzene, which are washed with hot water and dried in a vacuum (440 g.; m. p. 77—80°). Distillation at 1 mm. gives a small fraction boiling below 180°, but the main fraction (240 g.) boils at 180—190° and melts at 81—89°. After crystallisation from light petroleum, the product is obtained in needles melting sharply at 89°. Pollak records m. p. 87—88°. The *potassium* salt is extremely soluble in cold water, and sparingly soluble in alcohol, which precipitates it in very fine prisms (Found in material dried at 155°: K, 22·6. $C_6H_3O_6ClS_2K_2$ requires K, 22·4%). The *amide* is readily soluble in hot alcohol and in water, slightly soluble in the cold solvents, and separates in minute needles, m. p. 206—207° (Found: N, 10·5. $C_6H_7O_4N_2ClS_2$ requires N, 10·4%).

Chlorobenzene-2 : 4 : 6-trisulphonic acid is most conveniently obtained, not according to Pollak, v. Fiedler, and Roth (*loc. cit.*), but by the preparation of phenol-2 : 4 : 6-trisulphonyl chloride by the action of chlorosulphonic acid on phenol at 145—155° after Pollak, Gebauer-Fülnegg, and Riesz (*Monatsh.*, 1926, **46**, 383). The phenol trisulphonyl chloride, when heated with phosphorus pentachloride, gives about a 10% yield of crude chlorobenzenetrisulphonyl chloride, m. p. 152—162°; this crystallises from light petroleum (b. p. 80—100°) in needles, m. p. 170° (recorded m. p., 170—171°) (Found: C, 17·5; H, 0·6. Calc.: C, 17·6; H, 0·5%). The *potassium* salt forms colourless needles, which are excessively soluble in water and sparingly soluble in alcohol (Found: K, 25·3. $C_6H_2O_9ClS_3K_3$ requires K, 25·1%). *Diphenylamine*-2 : 4 : 6-*trisulphonanilide* is made by boiling the sulphonyl chloride and an excess of aniline together for 1 hour. Aniline hydrochloride is removed; the residue crystallises from nitrobenzene in light grey needles which darken on keeping, m. p. 227° (decomp.). When heated with sodium, it gives a fine violet colour (Found: C, 56·4; H, 4·1. $C_{30}H_{26}O_6N_4S_3$ requires C, 56·8; H, 4·1%).

1-Chloro-2-nitrobenzene-4-sulphonic acid is best obtained pure, not by nitrating the chlorobenzenesulphonic acid (compare Fischer, *Ber.*, 1891, **24**, 3188), but as follows: A mixture of chloro-

benzene-*p*-sulphonyl chloride (20 g.), nitric acid (20 c.c.; *d* 1·50), and concentrated sulphuric acid (80 c.c.) is stirred and warmed initially at 35°, when the reaction begins, and then for 5 hours at 25—30°. The product is precipitated by water, washed free from acid, and crystallised from light petroleum (b. p. 40—60°); it then has the correct m. p., 39—40°. The yield is 17 g. The *potassium* salt forms long, colourless needles readily soluble in hot, moderately easily soluble in cold water (Found in dry salt: K, 14·2 $C_6H_3O_5NClSK$ requires K, 14·2%).

Chlorobenzene-*p*-sulphinic acid was prepared in excellent yiel by reduction of the corresponding sulphonyl chloride with sodium sulphide after the method of D.R.-P. 224019 and purified by con version into the sparingly soluble ferric salt and crystallisation o the moderately soluble *ammonium* salt (shining plates). The aci melts at 100—102° (Otto and Brummer, *Annalen*, 1867, **143**, 113 give m. p. 88—90°) (*Found* for the ammonium salt dried over phos phoric oxide: N, 6·6; loss at 100°/40 mm., 8·4. $C_6H_8O_2NClS,H_2O$ requires N, 6·6; H_2O, 8·5%).

Carboxylic acids. Commercial *p*-chlorobenzoic acid was purifie until the correct melting-point was attained. It was finally foun more convenient, in order to obtain a pure specimen (m. p. 243 in a sealed tube), to prepare it from pure *p*-chlorotoluene. Th 4-chloro-3-nitrobenzoic acid (Schuchardt) melted at 182° before an after purification.

4-Chloro*iso*phthalic acid is best prepared by the oxidation o 4-chloro-*m*-xylene (b. p. 181—185°) as described for the preparatio of chlorotrimesic acid below. It is not essential in this case to extrac the acid with ether, as it is only slightly soluble in cold wate (Found: equiv., 100·6. Calc.: equiv., 100·25). It melts a 295°, the m. p. recorded by Ullmann and Uzbachian (*Ber.*, 190 **36**, 1799). No improvement in the yield followed the use of magne ium sulphate in the oxidation, which these authors advocate i order to minimise the hydrolysis of the chlorine atom in the chlor *iso*phthalic acid as the latter is produced.

1-Chlorotrimesic acid has already been prepared by the action phosphorus pentachloride on hydroxytrimesic acid (Ost, *J. pr. Chem* 1877, **15**, 308), but is much more conveniently made as follow Chloromesitylene is prepared by the chlorination of mesitylene presence of antimony trichloride at 10—30°, and the fraction boili at 204—206° (15·5 g.) is oxidised with potassium permangana (95 g. in 2200 c.c. of water) for 22 hours. The solution is conce trated, the unchanged chloromesitylene distilling over in the proce sulphur dioxide is passed in until the manganese dioxide has d appeared, and the carboxylic acid is collected after cooling. T

filtrate is extracted with ether, and the total yield is 15·5 g. (63·5%) of anhydrous acid, m. p. 285° (Ost gives 278°). It is very readily soluble in cold (contrast Ost) and excessively soluble in hot water (Found: equiv., 81·8. Calc.: equiv., 81·5). The oxidation was carried out also in presence of excess of magnesium sulphate, but there was no improvement in the yield. The hydrolysis without magnesium sulphate must have been very minute, since it could not be detected by a colour reaction with ferric chloride solution.

Details of the Methods used in Estimating the Amount of Hydrolysis.

All the reagents, organic and inorganic, were proved to be free from halogen. No halogen is detectable in Merck's guaranteed potassium hydroxide. The vessels were boiled with pure potassium hydroxide solution until all adventitious halogen was removed.

An aqueous-alcoholic solution was used (except where stated otherwise), because a medium was required which would dissolve both nitro-compound and potassium salt. Absolute alcohol, practically free from acetaldehyde, was diluted with the required amount of $N/2$-potassium hydroxide until the solution contained 60% of alcohol by volume on the assumption that no change in volume had occurred during mixing. Such a solution boils at about 82°. Richardson (J., 1926, 525, 528) has shown that in the prolonged treatment of *p*-chloronitrobenzene with alcoholic potassium hydroxide the nitro-group as well as the chlorine atom is apt to be attacked to form some dichloroazoxybenzene. However, the use of this reagent was continued, because the nitro-compounds (picryl chloride and 2 : 4-dinitrochlorobenzene) through which comparisons were made with sulphonic and carboxylic acids were heated for a relatively short time (15 minutes).

The equation $RCl + 2KOH = ROK + KCl + H_2O$ requires two mols. of potassium hydroxide. Three mols. were taken (except in Series III and IV, where only two were employed) in order to have a large excess of alkali always present; in the case of the nitro-compounds this was particularly necessary, as the speed of hydrolysis was so great.

The chloro-compound was refluxed with the potassium hydroxide solution in a Duroglass bromine flask adequately protected from acid fumes, and the amount of potassium chloride produced was estimated as silver chloride. The chlorine in chlorobenzene-*p*-sulphonic acid and in *p*-chlorobenzoic acid was not reactive enough at ordinary pressures, and high temperatures and sealed tubes were resorted to (Series I). The di- and tri-substituted chlorobenzene derivatives gave, after prolonged refluxing, sufficient chloride to be estimated by the micro-method.

Estimation of Chlorine.—After the reaction had proceeded for the desired time, the potassium hydroxide solution was acidified with concentrated nitric acid and filtered cold through a halogen-free Hirsch funnel and filter-paper, which retained certain products from the glass and also any unchanged precipitated carboxylic acid. A micro asbestos filter tube was then prepared after Pregl, but in addition the asbestos was thoroughly washed with hot aqueous ammonia solution, and then consecutively with water, dilute nitric acid, and alcohol. The chloride produced in the reaction was collected as silver chloride in the filter tube after Pregl. The silver chloride was often violet and was sometimes mixed with a relatively large amount of unchanged carboxylic acid, especially *p*-chlorobenzoic acid, the solubility of which in water at the ordinary temperature is less than 0·02. The substance in the filter was treated with a definite amount (which should be the same in all these cases) of hot 3% pure ammonia solution, and then the filtrate with water, dilute nitric acid, and alcohol. The precipitated silver chloride now coagulated more rapidly than before, and was again collected and weighed. (It is not easy to make micro asbestos filter tubes perfectly constant in weight to washing with ammonia, but any errors introduced through this are of the second order.) This gravimetric process, though tedious, is preferable to the volumetric methods for the estimation of several mg. of chloride.

SERIES I. *Compounds of formula* (I).

Activating group (X).	Temp.	Time (hrs.).	G.-mol. of subs.	G. of AgCl or c.c. of $AgNO_3$ soln.	% Conversion.	Ratio (CO_2H = 1).
NO_2	82°	6	0·0100	0·2548	17·8	
,,	82	6	0·0100	36·89 c.c.	18·4	
SO_3H (a)	160—170	5	0·0100	0·0600	4·18	1·035
,, (b)	140—165	10	0·004816	9·51 c.c.	3·94	2·03
,, (c)	100—170	36	0·005 *	0·00622	0·868	2·765
,, (d)	100—150	36	0·005 *	0·00246	0·3433	3·1
SO_2H (a)	160—170	5	0·0100	0·1217	8·48	3·93
,, (b)	140—165	10	0·005	17·82 c.c.	7·11	3·66
,, (c)	100—170	36	0·003 *	0·00731	1·70	5·41
CO_2H (a)	160—170	5	0·0100	0·0309	2·156	1
,, (b)	140—165	10	0·005	4·76 c.c.	1·94	1
,, (c)	100—170	36	0·00566 *	0·00255	0·3143	1
,, (d)	100—150	36	0·00671 *	0·00106	0·1103	1

* In aqueous solution.

0·01994*N*-Silver nitrate was used with thiocyanate, except in the second experiment, where 0·05003*N*-silver nitrate was used with potassium chromate as indicator.

In experiments (a) and (b) macroanalysis was used.

Except in the first two experiments (with *p*-chloronitrobenzene), he reactants were heated in red-line Jena glass tubes in a Lothar Meyer bomb furnace at temperatures varying from 100° to 170°. The temperatures varied very considerably owing to changes in the gas pressure, but this is immaterial, as the tubes were always in the urnace together. No doubt there were slight inequalities in the heating of the furnace, but the tubes were arranged in the furnace n different order in different experiments without causing great variations in the amount of hydrolysis. The experiments clearly how that there is a detectable order in the activation due to the different groups.

Temperatures higher than 170° were not employed, because at his temperature very minute traces of sulphuric acid were formed n the tubes containing sulphonic acid. In all the experiments nvolving sulphonic acids, the filtrate from the silver chloride was ested with barium nitrate: positive results for sulphuric acid were btained only in the products from these high-temperature experiments.

SERIES II. Compounds of formula (IV).

r denotes the amount of first-hour conversion compared with that of *o*-chloronitrobenzene (X nil).

Activating group (X).	Time (hrs.).	G.-mol. of subs.	G. of AgCl or c.c. of $AgNO_3$ soln.	% Conversion.	Ratio (CO_2H = 1).	*r*.
Nil	1	0·0100	0·0215	1·50		1·0
,,	6	0·0100	0·1195	8·3		
,,	6	0·0100	0·1208	8·4		
NO_2	0·25	0·0100	1·4254	99·4		
,,	0·25	0·0100	1·4288	99·6		
SO_3H (a)	1	0·0101	0·3513	24·06	3·79	16
,, (b)	6	0·00567	0·5740	70·6	2·49	
,, (c)	6	0·0101	66·59 c.c.	66·4	2·67	
CO_2H (a)	1	0·0100	0·0910	6·35	1·0	4·4
,, (b)	6	0·0100	0·4061	28·35	1·0	
,, (c)	6	0·0100	25·02 c.c.	24·9	1·0	

All these experiments were done at 82° with aqueous-alcoholic potassium hydroxide. 0·0997*N*-Silver nitrate was used with hiocyanate, but the process was not satisfactory, as the colour of he organic solution somewhat masked that of the indicator.

The ratio 3·79 for 1 hour is in fair agreement with the ratio for 6 hours, for if 24% of the sulphonic acid and 6·3% of the carboxylic cid present are converted per hour, then 80·7% and 32·3%, espectively, are transformed after 6 hours. This gives the ratio after 6 hours as 80·7/32·3 = 2·50 (Found: 2·49 and 2·67). This method is obviously very rough, but does not assume the order of he reaction.

Similar experiments for 1 hour were done in aqueous potassium hydroxide solution at 100°: the percentage conversion of the sulphonic acid was 20·6 and 19·2, and of the carboxylic acid, 5·2. Notwithstanding the higher temperature, the velocity of reaction is less in water than in alcohol. Similar cases are recorded in the literature (compare Slator and Twiss, J., 1909, **95**, 99; Rheinlander, J., 1923, **123**, 3105).

SERIES III. Compounds of formula (II).

Activating groups (X).	Time (hrs.).	G.-mol. of subs.	AgCl formed (g.).	Conversion in 127 hours per 0·01 g.-mol.	Conversion per 100 hours.	% Conversion per 100 hours.	*s*.
$2SO_3H$ (a)	63·5	0·01	0·0052	0·0104	0·0082	0·57	2·7
,, (b)	127	0·005	0·007025	0·01405	0·01107	0·77	4·0
,, (c)	127	0·005	0·00308	0·00616	0·00485	0·34	2·8
$2CO_2H$ (a)	63·5	0·01	0·00191	0·00382	0·00302	0·21	1 (a)
,, (b)	127	0·005	0·001715	0·00343	0·00270	0·19	1 (b)
,, (c)	127	0·005	0·00106	0·00212	0·00168	0·12	1 (c)

SERIES IV. Compounds of formula (III).

Activating groups (X).	Time (hrs.).	G.-mol. of subs.	AgCl formed (g.).	Conversion in 127 hours per 0·01 g.-mol.	Conversion per 100 hours.	% Conversion per 100 hours.	*s*.
$3SO_3H$ (a)	63·5	0·005	0·00821	0·03284	0·02583	1·80	1·7
,, (b)	127	0·0025	0·00791	0·03164	0·02491	1·74	1·4
,, (c)	127	0·0025	0·01102	0·04408	0·03472	2·42	2·7
$3CO_2H$ (a)	63·5	0·0025	0·00246	0·01968	0·01553	1·08	1 (a)
,, (b)	127	0·0025	0·00572	0·02288	0·0180	1·26	1 (b)
,, (c)	127	0·0025	0·00411	0·01644	0·0129	0·090	1 (c)
Alcoholic potassium hydroxide at 82°.							
$3SO_3H$	96	0·00679	0·0537			5·7	
Picryl chloride	0·25	0·01	1·4254	99·4% converted in 0·25 hour.			
,,	0·25	0·01	1·4288	99·6% converted in 0·25 hour.			

Weights of silver chloride, when given to the fourth decimal place only, were determined on a macro-balance.

It was found impossible to repeat, even approximately, the results of experiments carried out at different times, probably owing to differences in boiling point due to changes in barometric pressure, or to changes in the intensity of light. These difficulties were partly overcome by carrying out four experiments (each set labelled a, b, and c) at the same time in absence of bright light. The figures in the last column (*s*) give the ratio of chloride produced from a sulphonic acid to chloride produced from the corresponding carboxylic acid: *e.g.*, the first figure is obtained thus: 0·57/0·21 = 2·7.

The agreement in the different series is poor and the analyst (W. D.) admits that the problem of carrying out reactions on a macro-scale and then estimating the minute quantity of product on a

nicro-scale has not yet been solved. Nevertheless a rough agreement among the results is discernible.

Discussion of Results.

A lower limiting value for the activation due to nitro-groups ompared with that due to carboxyl or sulphonic acid groups can be btained. It has been shown that the chlorine in chlorobenzene- : 4-disulphonic acid is hydrolysed to the extent of about 0·57% n 100 hours (estimation of the hydrolysis for one time interval rom the amount produced during another is justifiable when the oncentration of the reactants is, as here, practically unchanged) n aqueous potassium hydroxide solution. 2 : 4-Dinitrochloro-enzene, on the other hand, is more than 99% hydrolysed in 0·25 our (see Series II) in alcoholic potassium hydroxide solution (which as been shown to have only a slightly greater hydrolytic power han the aqueous solution ; see p. 1130 and Series IV). Then, a direct roportion gives about 70,000 hours as the time required for 99% ydrolysis of chlorobenzene-2 : 4-disulphonic acid. This of course gnores the immense retardation of hydrolysis as the concentration f the reactants becomes less, and the figure is much more probably t least of the order of 10^6 instead of about 10^5. Similarly, by using he value 0·2% hydrolysis per 100 hours for chlorobenzene-2 : 4-licarboxylic acid, about 200,000 hours would be required for 99% ydrolysis. It may safely be said, then, that the nitro-groups in : 4-dinitrochlorobenzene have more than 70,000 and 200,000 times he activating effect of the acigenic groups in chlorobenzene-2 : 4-lisulphonic and chlorobenzene-2 : 4-dicarboxylic acids, respectively.

A comparison of the activating powers of the sulphonic and arboxylic acid groups is less indefinite. The first, third, and ourth series show the ratio of the effect of the sulphonic to that f the carboxylic acid groups to be 2—3, about 3, and about 2, espectively. The sulphinic acid group has been shown (Series I) o have about four times the effect of a carboxylic acid group under the same conditions. It is possible, however, that the relatively nstable sulphinic acid has decomposed in other directions to some xtent. This possibility is advanced, since we isolated a very small uantity of *p*-chlorophenyl disulphoxide, m. p. 137° (Otto, *loc. cit.*, ecords 136—138°), during the purification of the *p*-chlorobenzene-sulphinic acid with ammonia.

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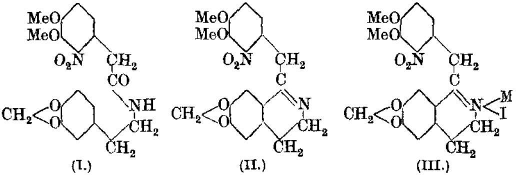
CXLIII.—*Synthetical Experiments on the Aporphine Group. Part II. A Synthesis of Bulbocapnine Methyl Ether.*

By JOHN MASSON GULLAND and ROBERT DOWNS HAWORTH.

THE synthesis of 5 : 6-dimethoxyaporphine described in Part I (this vol., p. 581) depended on the discovery of experimental conditions which allowed the Bischler–Napieralski synthesis to be utilised in the preparation of 1′-nitrobenzyl-3 : 4-dihydro*iso*quinoline bases. The present communication contains an account of an extension of the method to the synthesis of bulbocapnine methyl ether (V).

2′-*Nitro-3′ : 4′-dimethoxyphenylaceto-*β*-3 : 4-methylenedioxyphenylethylamide* (I) was prepared by condensing β-piperonylethylamine and 2-nitro-3 : 4-dimethoxyphenylacetyl chloride (Kay and Pictet, J., 1913, **103**, 952). By treating a cold chloroform solution of the amide (I) with phosphorus pentachloride, a good yield of *2′-nitro-3′ : 4′-dimethoxy-6 : 7-methylenedioxy-1-benzyl-3 : 4-dihydro*iso*quinoline* (II) was obtained. This pale yellow crystalline base, which yielded a sparingly soluble, almost colourless, crystalline *hydrochloride*, did not undergo atmospheric oxidation. When heated in a sealed tube at 100° with methyl iodide, the base (II) was converted into the *methiodide* (III); this yielded oxyhydrastinine and 2-nitrohomoveratrole on heating with dilute alkali.

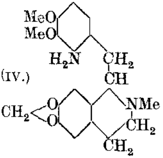


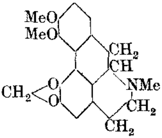
(I.) (II.) (III.)

The methiodide (III), in strongly acid solution, was reduced with zinc dust to *2′-amino-3′ : 4′-dimethoxy-6 : 7-methylenedioxy-1-benzyl-2-methyltetrahydro*iso*quinoline* (IV), which, although itself an oil, yielded a *crystalline dihydrochloride*. The addition of sodium nitrite to a solution of the base (IV) in dilute hydrochloric acid yielded a diazo-solution, which coupled with alkaline β-naphthol. These facts support the constitution assigned to the base (IV) and exclude the possibility of indole formation, which was observed in Part I of this series (pp. 584, 587).

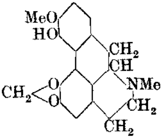
The phenanthrene ring-closure was effected by diazotising the base (IV) in a mixture of methyl alcohol and $2N$-sulphuric acid, but considerable difficulty was experienced in the isolation of the *dl*-bulbocapnine methyl ether from the reaction mixture. Previously it had been possible to isolate the aporphine bases in the form of their sparingly soluble hydrochlorides, but the solubility of the hydrochloride of *dl*-bulbocapnine methyl ether precluded the use of this method. Eventually the alkaloid was isolated in the form of a crystalline *hydriodide*, from which *dl*-bulbocapnine methyl ether (V) was liberated by the action of sodium hydroxide.

(IV.)





(V.)



(VI.)

The synthetical base crystallised from ether in well-defined rhombs, m. p. 135°, which were identical with a specimen of *dl*-bulbocapnine methyl ether, prepared from natural *d*-bulbocapnine as described by Gadamer (*Arch. Pharm.*, 1911, **249**, 508). Its colour reactions and *methiodide* also were indistinguishable from those of *dl*-bulbocapnine methyl ether prepared from naturally occurring *d*-bulbocapnine.

As Gadamer (*loc. cit.*, p. 509) has resolved *dl*-bulbocapnine methyl ether into its optically active modifications, this synthesis of the *dl*-form completes the synthesis of *d*-bulbocapnine methyl ether. The structure of *d*-bulbocapnine is therefore now limited to one of the two formulæ which are obtained by replacing one of the methoxyl groups in structure (V) by the hydroxyl group. Gadamer (*loc. cit.*) has selected formula (VI) as the more probable constitution of bulbocapnine, and we are engaged in an attempt to synthesise this base.

EXPERIMENTAL.

2-Nitro-3 : 4-dimethoxyphenylacetyl Chloride.—2-Nitroveratraldehyde was prepared as described by Pisovschi (*Ber.*, 1910, **43**, 2137), and was converted into 2-nitro-3 : 4-dimethoxyphenylacetic acid by the method of Kay and Pictet (*loc. cit.*). No attempt was made to purify the intermediate products, and the following description indicates briefly the modifications which were adopted in the preparation of large quantities of the acid. 2-Nitroveratraldehyde was subjected to the action of alcoholic potassium hydroxide as

described by Kay and Pictet, and the mixture was poured into water and extracted thoroughly with benzene. After being washed with sodium bisulphite solution, the extract was dried with sodium sulphate, and the benzene removed. The residual 2-nitro-3 : 4-dimethoxybenzyl alcohol, which solidified on cooling, was converted into the corresponding chloride by the action of phosphorus pentachloride in benzene solution; the benzene and phosphorus oxychloride were removed under diminished pressure, and the crude chloride which remained was converted into the corresponding cyanide as described by Kay and Pictet. The excess of alcohol was removed by distillation, water was added, and the cyanide extracted with benzene; the extract was dried with sodium sulphate and the benzene removed. The residual oil was sufficiently pure for conversion into 2-nitro-3 : 4-dimethoxyphenylacetic acid, more especially as the separation of the imino-ether hydrochloride provided a convenient purification.

2-Nitro-3:4-dimethoxyphenylacetic acid (5 g.), chloroform (20 c.c.), and thionyl chloride (3 c.c.) were warmed for 1 hour on the water-bath. The solvent was removed in a vacuum, and the residual 2-nitro-3 : 4-dimethoxyphenylacetyl chloride, which solidified on cooling, was employed without further purification for the following experiments.

2′-Nitro-3′ : 4′-dimethoxyphenylaceto-β-3 : 4-methylenedioxyphenylethylamide (I).—2-Nitro-3 : 4-dimethoxyphenylacetyl chloride (from 6 g. of acid) in benzene (30 c.c.) was gradually added to a cooled solution of β-piperonylethylamine (5 g.) in benzene (20 c.c.), which was constantly shaken, and the buff-coloured precipitate which separated was decomposed by the addition of 10% sodium hydroxide solution. The amide (I), which rapidly separated from the benzene, was collected, combined with a small second crop obtained by concentrating the benzene layer of the filtrate, and crystallised from ethyl alcohol; it formed colourless needles (8 g.), m. p. 158° (Found: C, 58·9; H, 5·4. $C_{19}H_{20}O_7N_2$ requires C, 58·8; H, 5·2%). This amide is sparingly soluble in light petroleum, ether, benzene, and cold methyl or ethyl alcohol, but readily soluble in chloroform.

2′-Nitro-3′ : 4′-dimethoxy-6 : 7-methylenedioxy-1-benzyl-3 : 4-dihydroisoquinoline (II).—Phosphorus pentachloride (6 g.) was added to a cooled solution of the amide (I) (5 g.) in chloroform (50 c.c.), and the mixture kept at room temperature for 36 hours, a pale yellow solid gradually separating. The chloroform and phosphorus oxychloride were removed under diminished pressure, the solid residue was extracted with much hot water and filtered off while hot from a small amount of tar, and the filtrate was made alkaline with ammonia. The dihydro*iso*quinoline (II) separated as a cream-coloured, amorph-

ous powder, which rapidly became crystalline. On recrystallisation from ethyl alcohol it formed pale yellow prisms (3·8 g.), m. p. 164° (Found: C, 61·6; H, 4·9. $C_{19}H_{18}O_6N_2$ requires C, 61·6; H, 4·9%). This base is sparingly soluble in light petroleum, ether, and cold methyl or ethyl alcohol and readily soluble in chloroform. The sparingly soluble *sulphate* and *nitrate* separate when the base is dissolved in dilute sulphuric and nitric acids respectively. When a solution of the base in hot dilute hydrochloric acid was cooled, the *hydrochloride* separated in very pale yellow plates, m. p. 230° (decomp.) (Found: C, 56·0; H, 4·8. $C_{19}H_{18}O_6N_2$,HCl requires C, 56·1; H, 4·7%).

*2'-Nitro-3' : 4'-dimethoxy-6 : 7-methylenedioxy-1-benzyl-3 : 4-dihydro*iso*quinoline Methiodide* (III).—The base (II) (3·2 g.) and methyl iodide (10 c.c.) were heated at 100° in a sealed tube for 1 hour and the excess of methyl iodide was then removed by distillation. The residue crystallised from rectified spirit in bright yellow needles, m. p. 215° (decomp.) (Found: C, 47·1; H, 4·2. $C_{20}H_{21}O_6N_2I$ requires C, 46·9; H, 4·1%). The methiodide (III) is sparingly soluble in water, methyl and ethyl alcohol. The methiodide (2 g.) and 5% sodium hydroxide solution (20 c.c.) were heated on a water-bath for 2 hours, and the colourless solution was subjected to steam distillation. The distillate was extracted with ether, the extract dried with sodium sulphate, and the solvent removed, leaving 2-nitrohomoveratrole as an oil. This was oxidised by a hot dilute solution of potassium permanganate to 2-nitroveratric acid, m. p. 201°, which was identified by comparison with a specimen prepared by the method of Pschorr and Sumuleanu (*Ber.*, 1899, **32**, 3409). The non-volatile portion was evaporated to dryness, and the solid residue extracted with chloroform. The residue from the dried, evaporated extract crystallised from aqueous alcohol in colourless needles, m. p. 98°. These were identified as oxyhydrastinine by comparison with a specimen of the latter prepared by the action of potassium hydroxide on hydrastinine (Freund and Will, *Ber.*, 1887, **20**, 2400; Freund, *Ber.*, 1889, **22**, 457).

*2'-Amino-3' : 4'-dimethoxy-6 : 7-methylenedioxy-1-benzyl-2-methyltetrahydro*iso*quinoline* (IV).—A suspension of the methiodide (III) (3·5 g.) in water (35 c.c.) and concentrated hydrochloric acid (70 c.c.) was heated on the water-bath and shaken vigorously while zinc dust (11 g.) was gradually added. A colourless crystalline salt gradually separated as the reduction proceeded. The hot solution was filtered, the residue thoroughly extracted with hot water, and the combined filtrate and washings made alkaline with ammonia and extracted with ether. The ethereal extract was dried with sodium sulphate, the ether removed, and the residual oil, which did not

crystallise, was dissolved in alcohol containing hydrogen chloride. The dihydrochloride of the base (IV), which rapidly separated, was collected (2·3 g.) and washed with alcohol. The *dihydrochloride* crystallised from alcohol, in which it is sparingly soluble, in colourless, glistening prisms, m. p. 231° (decomp.) (Found in materia' dried at 110°: C, 56·2; H, 6·0. $C_{20}H_{24}O_4N_2$,2HCl requires C, 55·9 H, 6·1%). The bright yellow solution obtained on addition o' sodium nitrite to the dihydrochloride in water gave, on treatmen with alkaline β-naphthol, a crimson azo-dye, which formed a deej magenta-coloured solution in concentrated sulphuric acid.

dl-*Bulbocapnine Methyl Ether* (V).—An ice-cold solution of th dihydrochloride (5·5 g.) of the base (IV) in sulphuric acid (27 c.c of 2*N*) and methyl alcohol (27 c.c.) was diazotised by the gradua addition of the calculated amount of 2*N*-sodium nitrite (freshl standardised). The bright yellow solution was heated on the watei bath for 40 minutes, and the deep-red solution obtained was reduce with zinc dust (3 g.) and concentrated hydrochloric acid (9 c.c. The hot liquid was filtered, the residue washed thoroughly wit boiling water, and the combined filtrate and washings were decon posed with ammonia and extracted with much ether; at this stag a considerable quantity of the amorphous dilaudanosine derivati separated. The pale yellow ethereal extract was washed with sodiu hydroxide solution and dried with sodium sulphate, and the eth removed. The residual oil was dissolved in dilute hydrochlo acid, and a concentrated solution of potassium iodide added; t hydriodide separated as a gum. The clear supernatant liquid w decanted, and the gum dissolved in hot alcohol; on cooling, *bulbocapnine methyl ether hydriodide* (1·2 g.) separated in alm colourless prisms, which darken at 240° and melt with decompositi at 250° (Found: C, 51·5; H, 4·9. $C_{20}H_{21}O_4N$,HI requires C, 51· H, 4·7%). *dl*-Bulbocapnine methyl ether was obtained as a g by decomposing a hot aqueous solution of the hydriodide w sodium hydroxide. This was extracted with ether, the extr dried with sodium sulphate, and the ether allowed to evapor slowly. dl-*Bulbocapnine methyl ether* separated in large, very p yellow rhombs, m. p. 135°, and no alteration was observed in melting point of a mixture of the synthetical base and a specin of *dl*-bulbocapnine methyl ether prepared from *d*-bulbocapnine described by Gadamer (*loc. cit.*). The synthetical base and specimen obtained from natural sources gave identical col reactions. They dissolved in concentrated sulphuric acid to f colourless solutions which rapidly became orange-red; they yiel deep red solutions with Erdmann's reagent, deep greenish-l colorations with Frohde's reagent, and with Mandelin's reage

red coloration was first produced, which rapidly became violet, then purple and finally blue. dl-*Bulbocapnine methyl ether meth-iodide* was prepared by heating the base with an excess of methyl iodide for 1 hour. The excess of methyl iodide was removed by distillation; the residue crystallised from methyl alcohol in long, colourless needles, m. p. 243° (Found : C, 52·5; H, 5·2. $C_{21}H_{24}O_4NI$ requires C, 52·4; H, 5·0%). The methiodide obtained from *dl*-bulbocapnine methyl ether of natural origin was prepared in a *similar manner, and no alteration was observed in the melting point* of a mixture of the methiodides obtained from the two sources.

Our thanks are due to Mr. D. G. P. Paterson, B.Sc., for help in some of the preparative work, and to the Research Fund Committee of the Chemical Society for grants.

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CXLIV.—*The Reaction of Bromine with Aliphatic Acids. Part II. The Relative Speeds of Bromination of Acetyl Bromide and Acetyl Chloride.*

By HERBERT BEN WATSON.

THE results of the author's investigation of the bromination of aliphatic acids (Part I; J., 1925, **127**, 2067) and anhydrides (Orton, Watson, and Hughes, J., 1927, 2458) have been interpreted by supposing that in both cases the change proceeds mainly through the acid bromide, the speed of bromination of which is assumed to be proportional to the concentration of the halogen. Such proportionality is indicated by the results of Urech (*Ber.*, 1880, **13**, 1688), and has now been confirmed by an examination of the bromination of acetyl bromide at 25° in an apparatus specially designed to avoid contact of the acid bromide with atmospheric moisture. With the acetyl bromide in excess, the values of $k_1 = 1/t \cdot \log a/(a-x)$ show a progressive decrease, but constants are obtained if allowance is made for the "fixing" of bromine in the equilibrium $HBr + Br_2 \rightleftharpoons HBr_3$ (compare Bugarsky, *Z. physikal. Chem.*, 1901, **38**, 561). The proportionality of the velocity to the concentration of bromine is in harmony with the suggestion (Orton, Watson, and Hughes, *loc. cit.*) that rapid enolisation is followed by a comparatively slow reaction with bromine. Small amounts of ferric chloride or sulphuric acid do not accelerate the reaction, but iodine bromide is a

catalyst; confirmation is thus obtained of the view previously expressed that the effect of the two first-named substances on the bromination of acetic anhydride is the result of an acceleration of the enolisation of the anhydride itself.

Bromine reacts with acetyl chloride more slowly than with acetyl bromide. At 25°, with the concentrations employed, the velocity is proportional to the concentration of bromine during the first half of the reaction, extensive perbromide formation being prevented by the reaction $HBr + CH_3 \cdot COCl = CH_3 \cdot COBr + HCl$ (Staudinger and Anthes, *Ber.*, 1913, **46**, 1417); the values of k_1 increase, however, as would be expected, when the amount of acetyl bromide becomes considerable. The mechanism of the reaction is probably similar to that suggested for the acid bromide, and the different speeds in the two cases may be attributed to the different "polar effects" of bromine and chlorine (Baker and Ingold, J., 1926, 2466; Ingold, *Chem. and Ind.*, 1926, **45**, 357). The comparatively slow rate of bromination of the acid chloride accounts for its inferiority to the acid bromide as an accelerator of the bromination of acids and anhydrides (compare Part I, p. 2074).

It has now been demonstrated that a carboxylic acid reacts with the bromide of another acid, $R \cdot CO_2H + R' \cdot COBr = R \cdot COBr + R' \cdot CO_2H$; on distilling molar quantities of bromoacetyl bromide and acetic acid, the first fraction boiled at 76—78° and gave the analysis of acetyl bromide; further, the freezing point of a solution of the same acid bromide in acetic acid indicated that the greater part had reacted after one hour at 25°.

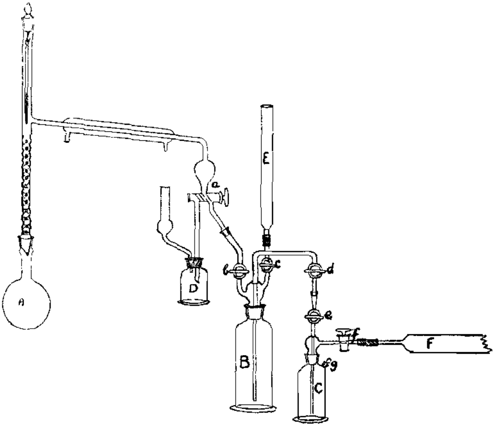
The observations described above provide further evidence in favour of the scheme put forward in Part I to represent the bromination of acetic acid and its homologues. The possibility of a reaction of bromine with the enolic form of the acid is not excluded, however, but, if such reaction occurs, the slowness of enolisation (compare Orton, Watson, and Hughes, *loc. cit.*) renders it imperceptible when even a small quantity of acid bromide is present (hence constant values of k_1; Part I, p. 2081). In presence of only a trace of the acid bromide, however, such as is probably produced by the introduction of hydrogen bromide (which will also accelerate the enolisation of the acid), the reaction may proceed to an appreciable extent through the enolide.

The vast difference in the speeds of bromination of acids and anhydrides is due mainly to the effect of the medium on the velocity of bromination of the acid bromide; for example, addition of only 1 c.c. of acetic anhydride to 30 c.c. of acetyl bromide results in a great increase in the speed of bromination, whereas at 25° the acid

bromide reacts with bromine only slowly in acetic acid solution, and not perceptibly in tetrachloroethane or carbon tetrachlorido (compare Ingold and Shoppee, this vol., p. 384). There is thus a complete analogy between the bromination of carboxylic acids and their anhydrides.

Experimental.

The purification and bromination of the acid halides were carried out in the apparatus shown in the figure, which consists of a flask, A,



with fractionating column and condenser, a bubbler B for collection of the pure halide, and a reaction vessel, C, all connexions being made of glass; a is a three-way tap, by means of which the distillate may be admitted either to the bubbler, B, or to the vessel D; when the three-way tap e is " closed " the reaction vessel, C, is shut off, and liquid allowed to drain away from the tube above e. Entry of moisture through the taps c and f is prevented by the phosphoric oxide tubes E and F. The thermometer is suspended from a glass hook fused on the glass stopper at the top of the column. The taps may conveniently be lubricated by liquid paraffin. Before the apparatus is used, the flask, A, is replaced by a phosphoric oxide

tube, and a slow current of air drawn through; the acyl halide is then distilled from A, the early and late fractions being delivered into D and the pure material into B. The desired quantity of liquid is transferred to the reaction vessel, C, by blowing dried air through c, and the reaction vessel is then disconnected from the remainder of the apparatus and placed in a thermostat at 25°. Bromine is introduced rapidly at g. For the purpose of withdrawing measured volumes of the reaction mixture, a ground-in pipette (capacity, 2·01 c.c.) is fitted in the aperture above the tap e, this tap is opened, and dried air blown in at f; e is then closed, the liquid in the pipette is allowed to fall to the mark and then delivered into an excess of aqueous potassium iodide, and the iodine is titrated with $N/10$-thiosulphate. In the tables which follow, time is expressed in minutes and titres in c.c. of $N/10$-thiosulphate.

Acetyl Bromide and Bromine.—The constants are calculated by a method similar to that employed by Bugarsky (*loc. cit.*). If $\{Br_2\}$ and $\{HBr\}$ represent total concentrations, and $[Br_2]$ and $[HBr]$ the concentrations of "unfixed" bromine and hydrogen bromide, then

$$K[HBr_3] = [Br_2][HBr] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$\{Br_2\} = [Br_2] + [HBr_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$
$$\{HBr\} = [HBr] + [HBr_3] \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

With the acetyl bromide in large excess, if a be the initial concentration of bromine, and x the amount of bromine which reacts with the acid bromide in time t, then, from the above equations, the concentration of "unfixed" bromine at time t will be

$$[Br_2] = \tfrac{1}{2}\{\sqrt{(K + 2x - a)^2 + 4K(a - x)} - (K + 2x - a)\},$$
$$\text{and } dx/dt = \frac{k}{2}\left\{\sqrt{(K + 2x - a)^2 + 4K(a - x)} - (K + 2x - a)\right\},$$

which, on integration, becomes

$$k = \frac{1}{2t}\left\{\frac{2(a + K)}{K} \cdot \log_e \frac{2a}{p} - \frac{2a + K}{K} \cdot \log_e \frac{2a + K}{p + K} - \frac{2a - p}{p + K}\right\}$$

where $p = \sqrt{(K + 2x - a)^2 - 2K(K + 2x - a) + 2K(a + K)} - (K + 2x - a)$

Pure AcBr.			AcBr + 0·035*M*-$FeCl_3$.			AcBr + 0·035*M*-H_2SO_4.		
t.	Titre.	*k.*	*t.*	Titre.	*k.*	*t.*	Titre.	*k.*
0	10·00		0	10·90		0	10·30	
60	8·75	0·0023	60	9·60	0·0022	60	9·00	0·0024
120	7·65	0·0024	120	8·40	0·0023	120	7·65	0·0027
240	5·95	0·0023	240	6·80	0·0021	240	6·85	0·0019
360	4·95	0·0024	360	5·60	0·0022	360	5·70	0·0019
540	3·90	0·0023	540	4·55	0·0021	540	4·05	0·0022

The somewhat irregular values of k when sulphuric acid is present are doubtless due to side reactions (compare Part I, p. 2070).

AcBr + 0·035M-IBr.			AcBr (30 c.c.) + Ac_2O (1 c.c.).		
t.	Titre.	k.	t.	Titre.	k.
0	10·10		0	10·35	
30	9·10	0·0037	60	6·60	0·0085
60	8·30	0·0036	180	3·20	0·0089
120	7·05	0·0033	240	2·60	0·0082
240	5·50	0·0030			
360	4·30	0·0030			

Acetyl Chloride and Bromine.—Values of $k_1 = 1/t \cdot \log a/(a - x)$.

t.	Titre.	k.	t.	Titre.	k.
0	10·45		540	6·55	0·00086
120	9·40	0·00089	720	5·40	0·00092
240	8·50	0·00086	1380	1·20	0·00157
360	7·70	0·00085			

Freezing Point of a Solution of Bromoacetyl Bromide in Acetic Acid.—0·9822 G. of the acid bromide was dissolved in 17·2668 g. of acetic acid of f. p. 16·5°. The theoretical f. p. of the solution if no reaction took place would be 15·4°, and if the acid bromide reacted completely ($CH_2Br{\cdot}COBr + CH_3{\cdot}CO_2H = CH_3{\cdot}COBr + CH_2Br{\cdot}CO_2H$) it would be 14·4°. Observed f. p.'s were 15·05°, 14·80°, and 14·60° after 15, 30, and 60 minutes, respectively, at 25°. Hence, proportion of acid bromide changed after 60 minntes = 80%.

In conclusion, the author wishes to express his appreciation of Professor Orton's interest in the work, and of a grant from the Chemical Society Research Fund which has largely defrayed the cost.

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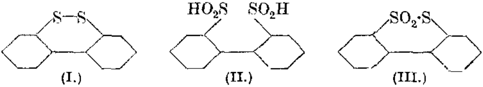
CXLV.—*Cyclic Disulphides derived from Diphenyl.*

By Harry James Barber and Samuel Smiles.

The mild treatment by which the dithio-group is formed from thiols seemed to offer favourable conditions for comparing the behaviour of the 4 : 4′-, 3 : 3′-, and 2 : 2′-dithioldiphenyls and their capacity to form cyclic disulphides. The experiments now described were originally planned for this purpose and with the object of providing information concerning the configuration of the diphenyl nucleus. In the meantime the supposed existence of the ring-compounds of benzidine has been clearly contradicted (Le Fèvre and Turner, J., 1926, 2476) and the stereochemistry of the diphenyl

nucleus has been further developed on other lines. The results now obtained accord with the evidence collected from these sources Simple ring-formation has not been observed with the 4 : 4'- and 3 : 3'-dithiols; the products obtained by the mild oxidation of these mercaptans are insoluble materials, evidently of high molecular weight, formed by the inclusion of more than one dithio group. On the other hand, simple ring closure of the 2 : 2'-dithiol is readily effected, the cyclic disulphide (I) being formed by oxidation. Also the 2 : 2'-disulphinic acid (II) has not been isolated

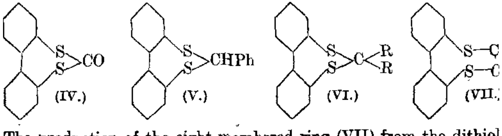


(I.) (II.) (III.)

owing to the ease with which it yields the cyclic *thiolsulphonate* (III) In comparison, the 4 : 4'-disulphinic acid is relatively stable.

2 : 2'-*Dithioldiphenyl* was obtained by the usual methods from the corresponding 2 : 2'-disulphonic acid, which in preliminary experiments was prepared from benzidine-2 : 2'-disulphonic acid (compare Limpricht, *Annalen*, 1891, **261**, 327), but subsequently sodium 2-iodobenzenesulphonate was used as a more convenient source. When a boiling aqueous solution of this substance was treated with copper, a good yield of the desired diphenyl derivative was obtained. *Sodium* 4-*iodotoluene*-3-*sulphonate* behaved similarly, but attempts to prepare the diphenyl-4 : 4'- and -3 : 3'-disulphonates from sodium 4- and 3-iodobenzenesulphonates, respectively, and the di-*o*-tolyl-4 : 4'-disulphonate from *sodium* 2-*iodotoluene*-5-*sulphonate* by this method were unsuccessful.

The formation of simple ring-systems from the 2 : 2'-dithiol is not confined to the six-membered disulphide (I); the *dithiolcarbonate* (IV), the *mercaptal* of benzaldehyde (V), and the *mercaptols* of acetone and benzil (VI) containing the seven-membered ring being obtained by the usual methods.



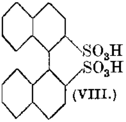
(IV.) (V.) (VI.) (VII.)

The production of the eight-membered ring (VII) from the dithiol and ethylene dibromide or oxalyl chloride was attempted without success.

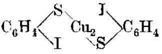
In the 1 : 1'-dinaphthyl series similar ring-formation has been

observed. When *sodium* 1-*iodonaphthalene*-2-*sulphonate* in boiling *aqueous solution* was submitted to the action of copper the 1 : 1′-*dinaphthyl*-2 : 2′-*disulphonate* (VIII) was obtained, but conversion of the chloride of this acid directly into the dithiol by reduction could not be effected owing to rupture of the dinaphthyl group; hence the required 1 : 1′-*dinaphthylene* 2 : 2′-*disulphide* (IX) was reached through the disulphoxide which resulted from the spontaneous decomposition of the unstable disulphinic acid.

When these disulphides are heated with copper their ring systems suffer contraction by loss of sulphur; *e.g.*, *diphenylene* 2 : 2′-*disulphide* (I) yielded dibenzthiophen, and 1 : 1′-dinaphthylene 2 : 2′-disulphide (IX) gave a dinaphthathiophen which must be regarded as 1 : 1′-*dinaphthylene* 2 : 2′-*sulphide*. This substance (m. p. 202°) is evidently different from that (m. p. 250°) obtained by Lanfry (*Compt. rend.*, 1911, **152**, 1254) from the interaction of sulphur and naphthalene; the constitution of the latter therefore remains uncertain.


(VIII.)

$$\begin{matrix} C_{10}H_6-S \\ | \quad\quad | \\ C_{10}H_6-S \end{matrix} \quad \text{(IX.)} \qquad \begin{matrix} S-C_6H_4I \\ | \\ S-C_6H_4I \end{matrix} \quad \text{(X.)}$$


(XI.)

A further point of interest was encountered in an attempt to obtain the cyclic disulphides by removing halogen from the *o*-iododisulphides (*e.g.*, X) with copper. Instead of the desired products, the corresponding thianthrens were isolated in good yield. Here the removal of iodine is evidently preceded by formation of the copper mercaptides (*e.g.*, XI), which subsequently lose cuprous iodide; this obvious interpretation was justified by the behaviour of the copper derivative of 2-iodophenyl mercaptan. This method of synthesis of thianthrens was realised in three cases, but it appears to be capable of wide application.

EXPERIMENTAL.

Sodium 2-Iodobenzenesulphonate.—The following improvement of the methods recorded (*e.g.*, Langmuir, *Ber.*, 1895, **28**, 95) for the preparation of this substance was used. A diazotised solution (500 c.c.) of aniline-*o*-sulphonic acid (32 g.) containing an excess of sulphuric acid was stirred and warmed with potassium iodide 42 g.). When decomposition was complete the solution was concentrated by evaporation, sulphurous acid being added at intervals to remove liberated iodine. The sulphonic acid which finally

separated from the cooled liquid was converted into the sodium salt (yield, *ca.* 80%). *Di-2-iodophenyl disulphide*, m. p. 133°, was obtained by usual methods (Found: C, 30·6; H, 1·7. $C_{12}H_8I_2S_2$ requires C, 30·6; H, 1·7%). 2-*Iodophenylmethylsulphone*, m. p. 109°, was obtained from the *sulphinic acid*, m. p. 108°, by alkaline methylation (Found: C, 29·8; H, 2·5. $C_7H_7O_2IS$ requires C, 29·8; H, 2·4%).

2-*Iodotoluene-5-sulphonic Acid.*—The moist diazo-compound resulting from 2-aminotoluene-5-sulphonic acid (10 g.) was added to potassium iodide dissolved in dilute sulphuric acid. The solution was gradually heated until it boiled and on cooling the required material separated. The *barium* salt was sparingly soluble in cold water [Found in air-dried sample: H_2O, 3·8. $(C_7H_6O_3IS)_2Ba,1\frac{1}{2}H_2O$ requires H_2O, 3·6%. Found in anhydrous sample: Ba, 18·8. $(C_7H_6O_3IS)_2Ba$ requires Ba, 18·7%]. The *chloride* of this acid had m. p. 61—62° (Found: C, 26·9; H, 2·0. $C_7H_6O_2ClIS$ requires C, 26·5; H, 1·9%) and the *amide* separated from alcohol in leaflets, m. p. 135°.

4-*Iodotoluene-3-sulphonic Acid.*—The moist diazo-compound resulting from 4-aminotoluene-3-sulphonic acid (20 g.) was added to a saturated solution of potassium iodide (20 g.) in dilute sulphuric acid. After the usual decomposition had been effected, the *potassium* salt of the required acid separated from the cooled liquid (Found in air-dried sample: H_2O, 5·1. $C_7H_6O_3ISK,H_2O$ requires H_2O, 5·1%. Found in anhydrous material: K, 11·4. $C_7H_6O_3ISK$ requires K, 11·6%). 4-*Iodotoluene-3-sulphonyl chloride* formed flat needles, m. p. 68°, from acetic acid (Found: C, 26·6; H, 1·9. $C_7H_6O_2ClIS$ requires C, 26·5; H, 1·9%) and the *amide* had m. p. 161—162°.

Di-4-iodo-m-*tolyl Disulphide*, $(C_6H_3MeI\cdot S\cdot)_2$.—When the sulphonyl chloride was reduced with zinc dust and mineral acid, iodine was removed. The *disulphide* was therefore prepared by reducing the crude sulphinic acid with hydrogen iodide in warm alcohol in presence of sulphurous acid. It was purified from acetone and had m. p. 104—105° (Found: I, 51·2; S, 12·7. $C_{14}H_{12}I_2S_2$ requires I, 51·0; S, 12·9%).

1-*Iodonaphthalene-2-sulphonic Acid.*—A cooled solution (2·5 l.) of sodium nitrite (12·6 g.) and sodium 1-aminonaphthalene-2-sulphonate (44·5 g.) was mixed with 60% sulphuric acid (50 c.c.). The sparingly soluble diazo-compound was collected and added to a cold solution of potassium iodide (40 g.) in dilute sulphuric acid; the mixture was then gradually heated. The required sulphonic acid, mixed with some alkali sulphonate, separated from the cooled solution (yield, about 50%). Further material obtained by evapor-

ating the liquors was generally very impure owing to extensive separation of iodine during the process. The *barium* salt separated from hot water in needles [Found: Ba, 17·2. $(C_{10}H_6O_3IS)_2Ba$ requires Ba, 17·1%].

1-*Iodonaphthalene*-2-*sulphonyl chloride*, m. p. 94°, formed needles from acetic acid (Found: C, 33·9; H, 1·8. $C_{10}H_6O_2ClIS$ requires C, 34·0; H, 1·7%) and was converted by alkaline sulphite into the sparingly soluble 1-*iodonaphthalene*-2-*sulphinic acid*, m. p. 143° (Found: C, 37·7; H, 2·5. $C_{10}H_7O_2SI$ requires C, 37·7; H, 2·2%). When a solution of the latter substance in hot alcohol was mixed with sulphurous acid and a few drops of hydriodic acid, *di*-1-*iodo*-2-*naphthyl disulphide* rapidly separated. This substance formed plates, m. p. 154°, from benzene (Found: C, 42·4; H, 2·3; I, 44·5; *M*, 575. $C_{20}H_{12}I_2S_2$ requires C, 42·1; H, 2·1; I, 44·5%; *M*, 570).

Derivatives of Diphenyl and Dinaphthyl.

Diphenyl-2 : 2′-*disulphonyl Chloride*.—A concentrated aqueous solution of sodium 2-iodobenzenesulphonate (20 g.) was boiled with finely divided copper (12 g.) and a small quantity of copper sulphate solution (1 c.c.). The progress of the removal of halogen was followed by the change in appearance or increase in weight of the copper powder; usually the process was complete in about 2 hours. The solution, after being freed from copper by hydrogen sulphide, was evaporated on the water-bath; the residue was dried at 150° and treated with phosphorus pentachloride (20 g.), giving the crude disulphonyl chloride (yield, about 75%). The purified material, m. p. 138° (Found: Cl, 20·5. Calc.: Cl, 20·2%), was identified with a sample prepared by the method of Limpricht (*loc. cit.*) from benzidine-2 : 2′-disulphonic acid. The dianilide, m. p. 186°, was obtained by heating the chloride with excess of aniline (Found: N, 6·2. Calc.: N, 6·0%).

Diphenylene 2 : 2′-*Disulphide* (I).—The crude diphenyldisulphonyl chloride contained a small quantity of the iodobenzenesulphonyl chloride, but since this impurity was easily removed during conversion into the thiol further purification of the chloride was not necessary. In the reduction of this dichloride the use of tin was avoided because of the formation of a very stable tin derivative of the dithiol; zinc dust and hydrochloric acid gave the best results, the procedure being that used by Zincke (*Ber.*, 1909, **42**, 3367). The required product was isolated by treating the reduction liquor with a current of steam, in which the dithiol was moderately volatile; any 2-iodophenyl mercaptan present was rapidly removed with the alcohol in the first portion of the distillate. The yields (50—60%) varied somewhat according to the amount under treat-

ment. In this way, 2 : 2′-*dithioldiphenyl* was obtained in needle of agreeable odour and m. p. 78—79° (Found : C, 66·0; H, 4·8 S, 29·7. $C_{12}H_{10}S_2$ requires C, 66·1; H, 4·6; S, 29·4%). Methy ation in alkaline media yielded 2 : 2′-dimethylthioldiphenyl (m. p 155°), which had been previously obtained by Brand (*J. pr. Chem* 1924, **107**, 358) from 2-iodophenyl methyl sulphide and copper.

2 : 2′-*Dicarboxymethylthioldiphenyl*, $(CO_2H{\cdot}CH_2{\cdot}S{\cdot}C_6H_4{\cdot})_2$, was ob tained from the thiol and sodium chloroacetate in alkaline media It separated from alcohol and water in plates, m. p. 201—202 (Found : C, 57·5; H, 4·3. $C_{16}H_{14}O_4S_2$ requires C, 57·5; H, 4·2%)

When a solution of the dithiol in warm alcohol was mixed wit an excess of alcoholic ferric chloride *diphenylene* 2 : 2′-*disulphid* immediately separated in almost theoretical yield. It forme yellow needles, m. p. 113°, from hot acetic acid (Found : C, 66·4 H, 3·8; S, 29·1; *M*, 208. $C_{12}H_8S_2$ requires C, 66·6; H, 3·7; S 29·6%; *M*, 216). When this substance was kept for 2 hours a 250° in presence of finely divided copper, dibenzthiophen wa formed. This was extracted from the reaction mixture with ho alcohol, purified, and identified with an authentic sample in th usual manner.

Diphenylene 2 : 2′-*Disulphoxide* (III).—(*a*) When a warm solutio of diphenylene 2 : 2′-disulphide (1 g.) in acetic acid (50 c.c.) wa slowly mixed with nitric acid (10 c.c.), oxidation took place and th required disulphoxide later separated in the crystalline state (*b*) The solution obtained from the interaction of the disulphony chloride and hot aqueous alkaline sulphite was mixed with exces of dilute mineral acid. The sulphinic acid which separated change spontaneously in the course of a few minutes to the cyclic *disulph oxide* (III). This crystallised from hot alcohol in needles, m. p 128° (Found : C, 57·9; H, 3·7; *M*, 237. $C_{12}H_8O_2S_2$ requires C 58·1; H, 3·2%; *M*, 248), and yielded the disulphide when reduce with hydriodic acid in warm acetic acid.

Diphenylene 2 : 2′-*Dithiolcarbonate* (IV).—A toluene solution o carbonyl chloride was gradually added to a stirred alkaline solutio of the dithiol until the latter was removed from the aqueous portio of the mixture. Evaporation of the toluene yielded the produc which, after crystallising from alcohol (charcoal), had m. p. 101·5 (Found : C, 63·8; H, 3·4; *M*, 235. $C_{13}H_8OS_2$ requires C, 63·9 H, 3·2%; *M*, 244).

The diphenyl-2 : 2′-mercaptals and -mercaptols were prepare from the dithiol and the requisite aldehyde or ketone in alcoho with the aid of hydrogen chloride. Separation of the require products was usually complete in about 12 hours (yields, 70—90%) In this way were obtained the *diphenylene*-2 : 2′-*mercaptal* of benz

aldehyde (V), m. p. 105—106° (Found : C, 74·2; H, 4·7; S, 20·8; *M*, 305. $C_{19}H_{14}S_2$ requires C, 74·5; H, 4·6; S, 20·9%; *M*, 306), the *diphenylene*-2 : 2'-*mercaptol* of acetone (VI), m. p. 95° (Found : C, 69·5; H, 5·8; *M*, 277. $C_{15}H_{14}S_2$ requires C, 69·7; H, 5·4%; *M*, 258), and the *diphenylene*-2 : 2'-*mercaptol* of benzil (VI), m. p. 198° (Found : C, 75·8; H, 4·6. $C_{26}H_{18}OS_2$ requires C, 76·1; H, 4·4%).

4 : 4'-*Dimethyldiphenyl*-2 : 2'-*disulphonyl Chloride*.—When sodium 4-iodotoluene-3-sulphonate was treated with copper and copper sulphate as described in the case of the 2-iodobenzenesulphonate, the halogen was removed. The crude product yielded the required *sulphonyl chloride* after the usual treatment. This substance formed needles, m. p. 117—118°, from acetic acid (Found : C, 44·0; H, 3·2; *M*, 387. $C_{14}H_{12}O_4Cl_2S_2$ requires C, 44·3; H, 3·2%; *M*, 379) and when it was treated with zinc and hydrochloric acid the ditolyl nucleus apparently suffered fission, since a 60% yield of *m*-tolyl mercaptan was isolated as the product. The latter substance was identified by comparing its *p*-nitrobenzoyl derivative with m-*tolyl* p-*nitrothiolbenzoate*, prepared from *m*-tolyl mercaptan and *p*-nitrobenzoyl chloride in quinoline, which crystallised from alcohol in pale yellow needles, m. p. 96° (Found : N, 5·3; *M*, 266. $C_{14}H_{11}O_3NS$ requires N, 5·1%; *M*, 273). The conversion of the disulphonyl chloride into the cyclic disulphide was not further pursued.

3 : 3'-*Dimethylthioldiphenyl*.—Benzidine-3 : 3'-disulphonic acid was converted into diphenyl-3 : 3'-disulphonyl chloride by Borsche's method (*Ber.*, 1917, **50**, 827). When this material was reduced with zinc dust and acid, the required dithiol was obtained as a pale yellow, viscous liquid which was not volatile in steam and was not obtained sufficiently pure for analysis. It was characterised by conversion into the *dimethylthiol*, which formed needles, m. p. 50°, from alcohol (Found : C, 67·7; H, 5·8. $C_{14}H_{14}S_2$ requires C, 68·2; H, 5·7%). The usual oxidising agents converted the dithiol into an amorphous material which was insoluble in organic solvents.

4 : 4'-*Dichlorodiphenyl*-3 : 3'-*disulphonyl Chloride*.—Replacement of the amino-groups in benzidine-3 : 3'-disulphonic acid was effected in the usual manner. After hydrochloric acid and copper had been removed from the solution of the chloro-acid, the solvent was removed and the residue was treated with phosphorus pentachloride. The crude *sulphonyl chloride* was purified from acetone and subsequently from acetic acid; it then melted at 179° (Found : Cl, 33·4. $C_{12}H_6O_4Cl_4S_2$ requires Cl, 33·8%). The dithiol obtained by the usual methods was a liquid and was characterised by conversion into 4 : 4'-*dichloro*-3 : 3'-*dimethylthioldiphenyl*, which crystallised

from alcohol in needles, m. p. 130° (Found: C, 53·8; H, 4·7; *M*, 308. $C_{14}H_{12}Cl_2S_2$ requires C, 53·3; H, 3·8%; *M*, 315). Treatment of the dithiol with ferric chloride or hydrogen peroxide gave an amorphous intractable material which was insoluble in organic solvents.

Diphenyl-4 : 4′-*disulphinic acid* was obtained (60% yield) by reduction of the 4 : 4′-disulphonyl chloride with boiling alkaline sulphite; it separated from hot water in needles, m. p. 143° (decomp.) (Found: C, 50·7; H, 3·8. $C_{12}H_{10}O_4S_2$ requires C, 51·0; H, 3·5%). In presence of mineral acid the substance was slowly converted into an amorphous material, presumably a disulphoxide of high molecular weight, which was insoluble in fused naphthalene or diphenyl. 4 : 4′-Dithioldiphenyl was prepared from the corresponding disulphonyl chloride; the formation of an amorphous insoluble material by oxidation of this according to Zincke (*Ber.*, 1912, **45**, 3466) was confirmed.

1 : 1′-*Dinaphthyl*-2 : 2′-*disulphonic Acid* (VIII).—The potassium salt of this acid was obtained by the action of copper powder on a boiling aqueous solution of potassium 1-iodonaphthalene-2-sulphonate in presence of a little copper sulphate. It separated from water in nacreous leaflets (Found: K, 15·5. $C_{20}H_{12}O_6S_2K_2$ requires K, 15·9%). The corresponding disulphonyl chloride was purified from acetic acid and had m. p. 202—203° (Found: C, 53·1; H, 2·7; Cl, 15·7%; *M*, 452. $C_{20}H_{12}O_4Cl_2S_2$ requires C, 53·2; H, 2·6; Cl, 15·7; *M*, 451). Reduction of this chloride with zinc dust and hydrochloric acid in the usual manner yielded 2-naphthyl mercaptan, which was identified as disulphide.

1 : 1′-*Dinaphthylene* 2 : 2′-*Disulphide* (IX).—The chloride slowly dissolved in hot alkaline sulphite, but when this solution was acidified a colourless material separated which was insoluble in dilute alkali. This, by analogy with the diphenyl derivative, was the disulphoxide; it was not further investigated, but was submitted to the action of hydriodic acid in warm acetic acid. The required cyclic *disulphide* was then obtained in bright yellow needles, m. p. 214°, which were purified from hot acetic acid (Found: C, 75·2; H, 4·0; *M*, 307. $C_{20}H_{12}S_2$ requires C, 75·9; H, 3·8%; *M*, 316). When this substance (0·5 g.) was kept at 250° for an hour with finely divided copper (0·15 g.) the sulphide of the metal was formed; from the product, hot benzene extracted 1 : 1′-*dinaphthylene* 2 : 2′-*sulphide*, which, on purification, formed leaflets, m. p. 202° (Found: C, 84·4; S, 10·7. $C_{20}H_{12}S$ requires C, 84·5; S, 11·2%).

Thianthren derivatives were prepared from *o*-iodo-disulphides by the action of copper powder as in the following typical experi-

ment. A mixture of di-*o*-iodophenyl disulphide (13 g.) and finely divided copper (8 g.) was heated at about 180° for ½ hour and the mass was cooled and extracted with chloroform; the crude material (yield, about 60%) was purified and then identified with an authentic sample of thianthren. In this way di-4-iodotolyl 3-disulphide yielded 2 : 6-dimethylthianthren (Fries and Volk, *Ber.*, 1909, **42**, 1175), identified as the disulphone, and di-1-iodonaphthyl 2-disulphide gave dinaphthathianthren (Fries and Volk, *loc. cit.*).

In conclusion, we desire to thank Dr. Child for a supply of iodonaphthyl sulphide and Mr. Wright for data concerning iodophenyl mercaptan. We also wish to thank the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in these experiments.

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CXLVI.—*The Photodecomposition of Triphenylmethyl.*

By SYDNEY THOMAS BOWDEN and WILLIAM JACOB JONES.

THE decolorisation of the free radical triphenylmethyl in direct sunlight was discovered by Gomberg and Cone (*Ber.*, 1904, **37**, 3545), who obtained as products of the reaction in benzene solution triphenylmethane, an oil, and at least two different solid substances. According to these investigators, photochemical decomposition in carbon tetrachloride solution proceeds much more rapidly than in benzene and takes a different course, an oil and a mixture of crystalline substances, but no triphenylmethane, being formed. They state that in diffused light solutions of triphenylmethyl suffer only traces of decomposition, even after being kept for longer than a year.

Schmidlin and García-Banús (*Ber.*, 1912, **45**, 1344) observed rapid and complete decolorisation of benzene solutions of the free radical even in diffused daylight, but only when the solution was optically pure and prepared in the cold by the action of molecular silver on triphenylchloromethane. The application of heat and the use of less noble metals gave yellow impurities, which were more stable in the light and masked the decolorisation of the free-radical solutions. It was in this manner that Schmidlin and García-Banús explained the contradiction between their observations and those of Gomberg and Cone; moreover, they showed that, under the action of light, triphenylmethyl in benzene solution decomposed quantitatively into triphenylmethane and diphenyl*bis*diphenylene-ethane.

The present investigation was undertaken (*a*) to ascertain whether ultra-violet light is active in effecting autoxidation and reduction of triphenylmethyl, (*b*) to determine the effective region of the visible spectrum in causing photodecomposition, and (*c*) to examine the behaviour of the free radical in various solvents.

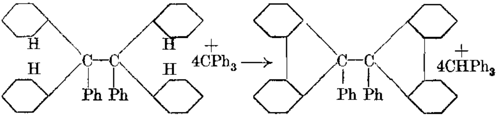
We have found that in ultra-violet light triphenylmethyl does not undergo appreciable autoxidation and reduction, either in the solid state or in solution in benzene. Furthermore, an irradiated system in which triphenylmethyl is being prepared by the agitation of mercury with a benzene solution of triphenylchloromethane gives the same characteristic yellow solution as a similar system which is not irradiated. We find also, in accordance with the results of Schmidlin and García-Banús, that solutions of triphenyl methyl are completely decolorised even in diffused daylight, and deposit crystals of diphenylbisdiphenylene-ethane. The decolorisation is observed to be complete even when mercury is employed in the preparation of the free radical. Moreover, a benzene solution of triphenylmethyl, prepared directly by agitating together pure mercury, benzene, and triphenylchloromethane (without previous isolation of the solid free radical), is similarly completely decolorised on exposure to sunlight. It would appear, therefore, that th cause of the contradiction between the observations of Gomber and Cone and those of Schmidlin and García-Banús is to be referre to the different intensities of light to which their respective prepar ations were exposed. In this connexion it is evident that the rat of photodecomposition in diffused light is considerably less tha that which obtains in direct sunlight, for in diffused light of lo intensity, solutions of triphenylmethyl may be kept for severa months without giving perceptible indication of loss in colour.

It has been ascertained that the region of the visible spectrum which is most active in effecting the photodecomposition is th green-blue, *viz.*, 5300—4000 Å.U. It is in this region that tr phenylmethyl exhibits strongest absorption (Meyer and Wielan *Ber.*, 1911, **44**, 2557), so that, in this case, it is the region of greate absorption which is the most photochemically active. In yello light triphenylmethyl does not undergo autoxidation and reductio In this connexion it may be mentioned that Luther and Plotniko (*Z. physikal. Chem.*, 1908, **61**, 524) showed that in the oxidatic of hydriodic acid by oxygen, the blue region of the spectrum most active, and that the ultra-violet rays are comparative ineffective.

The exposure of 2% triphenylmethyl solutions to direct su light (in April) results in their complete decolorisation in abo 3 hours, and in the subsequent deposition of crystals of diphen

bisdiphenylene-ethane. Very frequently deposition of the latter compound occurs before the solution is completely decolorised. When the solution of the free radical is agitated during exposure, decolorisation naturally proceeds more rapidly, owing to the fact that fresh layers of the solution are exposed to the light. The presence of triphenylmethyl peroxide or triphenylchloromethane causes no change either in the course or in the products of the reaction.

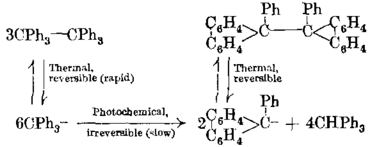
Schmidlin and García-Banús (*loc. cit.*) regard the easily dissociated hexaphenylethane as being oxidised by the triphenylmethyl to the difficultly dissociated diphenylbisdiphenylene-ethane, and formulate the photochemical change as follows:



On the basis that the valences of the atoms in the triphenylmethyl complex possess different polarities, Fry (*Z. physikal. Chem.*, 1915, **90**, 458) has given a specific interpretation of this reaction in terms of the electronic conception of positive and negative valences.

The chemical and physical properties of solutions of hexaphenylethane are most readily explained on the Gomberg theory, which postulates the dissociation and isomerisation of the fully saturated hydrocarbon. In view of this, it becomes of interest to inquire into the reaction mechanism of the photodecomposition. In benzene at the temperature of the irradiation experiments, the degree of dissociation of the hexa-arylethane, and consequently, the amount of unimolecular form present, is of low order. However, the extreme mobility of equilibration is shown by the marked reactivity of the solutions, for under ordinary conditions the main constituent of the solution is the bimolecular form. Inasmuch as it is improbable that irradiation of the system will influence materially the degree of dissociation of the bimolecular form, it would appear that the photochemical reaction is to be regarded as occurring in the first place between the products of thermal dissociation. Furthermore, in view of the fact that the photochemical change involving the unimolecular forms proceeds considerably more slowly than the equilibration of the system, it follows that the former reaction will determine the measured rate of photodecomposition. One of the final products of the reaction,

viz., diphenylbisdiphenylene-ethane, is likewise slightly dissociated in solution. On the assumption that the first product of photochemical change is phenyldiphenylenemethyl, which subsequently undergoes association to the corresponding bimolecular form, the complete scheme for the photochemical autoxidation and reduction of hexaphenylethane solutions may be represented as follows :



For simplicity of representation, no distinction is made in the above scheme between the benzenoid and the quinonoid forms, but on the assumption that both forms are photosensitive to a particular range of frequencies it is extremely improbable that they will be photosensitive to the same degree. Under these conditions, the irradiation of a system containing hexaphenylethane effects the photochemical transformation of one or both types of radicals into phenyldiphenylenemethyl and triphenylmethane. As a result, simultaneous dissociation of the bimolecular hexaphenylethane and association of phenyldiphenylenemethyl to diphenylbisdiphenylene-ethane occurs, so that complete transformation of the first into the last two is ultimately realised. Inasmuch as there are present two types of " odd " molecules, *viz.*, triphenylmethyl and phenyldiphenylenemethyl, the possibility of inter-association of these two radicals to give the mixed bimolecular form, $CPh_3{-}CPh{<}{}^{C_6H_4}_{C_6H_4}$, has to be considered. Since the final products of the reaction are diphenylbisdiphenylene-ethane and triphenylmethane, it follows that the mixed form does not have a stable existence under the conditions of the experiment.

The nature of the solvent is found to exert a marked influence on the rate of decolorisation. In the case of non-ionising solvents we find that photochemical change proceeds in all such solvents investigated. On exposing 2% solutions of triphenylmethyl in benzene, toluene, *m*-xylene, mesitylene, and hexane to direct sunlight, decolorisation is observed to be most rapid in hexane. The decolorisation proceeds rapidly in mesitylene also, whereas in *m*-xylene and in toluene the rate of loss in colour is slower, but still more rapid than in benzene.

The photochemical behaviour of triphenylmethyl in a com-

paratively weakly ionising solvent, such as liquid sulphur dioxide, is entirely different from that in the ordinary non-ionising solvents. When solutions of triphenylmethyl in sulphur dioxide are exposed to light, no indication of photochemical autoxidation is observed. There is no loss in colour after several hours' exposure to sunlight. Furthermore, on exposure to light there is no appreciable change in the conductivity of the solution. This points to the fact that the state of triphenylmethyl in a dissociating solvent is essentially of different character from that existing in non-ionising media.

Although hexaphenylethane in non-ionising solvents exhibits no appreciable conductivity, it has been shown by Walden (*Z. physikal. Chem.*, 1903, **43**, 385) and by Gomberg and Cone (*Ber.*, 1904, **37**, 2043) to behave as an electrolyte in liquid sulphur dioxide. Moreover, the absorption spectrum of triphenylmethyl in non-ionising solvents is different from that in liquid sulphur dioxide (Meyer and Wieland, *Ber.*, 1911, **44**, 2557). The several theories which have been advanced to explain the conductance of triphenylmethyl in sulphur dioxide can also be applied in a general way to account for the photochemical inactivity of the compound in this solvent. At the present time none of these theories is entirely satisfactory. Consideration of the stability of the possible molecular complexes formed between triphenylmethyl and the solvent leads to the conclusion that the photochemical behaviour cannot be materially influenced in this connexion. In the case of sulphur dioxide solutions, if we assume a direct solvation of hexaphenylethane, it is probable that such a solvate would not differ greatly in photochemical behaviour from that of the addition complexes present in the ordinary organic solvents. The complete inhibition of the reaction must be due to the absence of the triphenylmethyl radical in equilibrium with hexaphenylethane. In any case, the photochemical behaviour of the free radical is shown to be entirely different from that of the triphenylmethyl ion, whether the latter be solvated or otherwise.

Even in the solid state, hexaphenylethane gives indications of being photosensitive. Although no change in melting point is observed when the substance is exposed to direct sunlight for several days, a slight loss in colour occurs. It is probable, however, that this is due to the presence of slight traces of adsorbed solvent.

EXPERIMENTAL.

Preparation of Triphenylmethyl.—Preliminary experiments carried out to ascertain the most suitable method of preparing triphenylmethyl showed that the method of Schlenk, Weickel, and Herzenstein (*Annalen*, 1909, **372**, 2) was unsuitable, owing to the relatively

high temperature required for the complete reduction of triphenylchloromethane by means of copper. The method of Schmidlin (*Ber.*, 1908, **41**, 423), which depends upon the interaction of magnesium triphenylmethyl chloride with triphenylchloromethane, was found to be far more convenient, but gave a product of uncertain purity owing to contamination with magnesium compounds. The method of Gomberg (*J. Amer. Chem. Soc.*, 1917, **39**, 1652; *Chemical Reviews*, 1924, **1**, 99) proved essentially suitable, but, owing to the possible sensitivity of the photochemical reaction under study to the presence of small amounts of impurities, we made the following modifications: (*a*) The reduction of the triphenylchloromethane to triphenylmethyl was effected in an all-glass vessel, from which the transfer of the solution to the concentrating apparatus took place out of contact with air; (*b*) the solution was filtered prior to concentration; (*c*) the removal of adherent solvent in the later stage of the preparation was carried out by the use of a heating bath of methyl alcohol vapour. Contact of the free radical solution with the stopcocks of the concentrating apparatus was minimised by a suitable device, and intrusion of air into the apparatus during the process of concentration under reduced pressure was effectively prevented by surrounding the top and bottom of the stopcocks with large rubber caps maintained inflated with carbon dioxide.

The carbon dioxide, which provided the inert atmosphere in all the experiments, was rigorously purified, and freed from traces of admixed oxygen by preliminary passage through a solution of triphenylmethyl in benzene. The calcium chloride used for drying the gas was recrystallised in an atmosphere of carbon dioxide, and then dehydrated in a stream of the same gas in order to effect complete removal of occluded oxygen. The acetone employed for crystallising the free radical was prepared in the pure state by the decomposition of its compound with sodium iodide (Shipsey and Werner, J., 1913, **103**, 1255), followed by dehydration and fractionation.

The solid free radical was deprived of traces of solvent in an apparatus designed to prevent undue local heating of the substance, and consisting of a long tube, closed at both ends with rubber stoppers, through which passed short exit tubes provided with stopcocks; one end of the tube was connected to the carbon dioxide generator, and the other to a suction pump and manometer. The long tube was surrounded by a jacket through which the vapour of boiling methyl alcohol was circulated. In this manner, the substance, contained in a porcelain boat placed in the inner long tube, was subjected to a process of solvent removal

under reduced pressure in a slow stream of carbon dioxide at a temperature slightly below the boiling point of methyl alcohol.

Irradiation Experiments with Ultra-violet Light.—For the investigation of the action of ultra-violet light on triphenylmethyl in the solid state, the material was contained in a small quartz vessel, and exposed for 5 hours to ultra-violet light from a carbon arc lamp provided with a quartz window: it presented no change in appearance or in melting point after the exposure.

Irradiation of the triphenylmethyl solutions was carried out in specially constructed quartz tubes. The apparatus employed for filling the tubes with solution enabled the operation to be conducted in the entire absence of air. In view of the extremely reactive nature of the radical, it was considered important to avoid contact of the solution with any contaminating surface during the exposure, and accordingly the quartz tubes were sealed off under reduced pressure in the oxy–coal-gas flame. The tubes, which had an approximately elliptical cross-section of long major axis, were closed at the bottom and provided with long, narrow constrictions. The sealing of the tubes was effected at a point sufficiently distant from the liquid surface to prevent undue heating of the solution. This precaution is necessary since triphenylmethyl solutions decompose on excessive heating (Wieland, *Annalen*, 1911, **381**, 200). Care was taken to remove the film of triphenylmethyl solution adhering to the constriction by washing it down several times with pure solvent prior to sealing, and the possibility of contamination of the solution with traces of the thermal-decomposition products of triphenylmethyl was thus avoided. The tubes were exposed with both their longitudinal axes and their longer cross-sectional axes at right angles to the direction of the ultra-violet radiation from a Cooper–Hewitt mercury lamp of fused quartz. The irradiation chamber in which the tubes were placed was cooled by currents of cold air, so that its temperature did not exceed 19°. After 60 hours' intermittent exposure to the ultra-violet radiation, the solution presented no change in appearance, and no perceptible decrease in the intensity of the characteristic yellow colour was observed on comparison with a control solution of the same concentration which had not been irradiated. A solution of triphenylmethyl containing, in the first instance, traces of oxygen likewise showed no loss in colour on exposure to ultra-violet light for 15 hours.

In order to ascertain whether autoxidation and reduction of triphenylmethyl in ultra-violet light took place during its formation from triphenylchloromethane, a 6% solution of the aryl chloride in benzene was introduced into a quartz tube of the form already

described; excess of pure air-free mercury was added, and the tube sealed. A control solution of the same concentration, together with the same amount of mercury, was also prepared and suitably protected from ultra-violet light. Both tubes were attached to a shaking machine, which effected gentle agitation of the contents whilst the arrangement was exposed to ultra-violet light from the mercury lamp. As agitation proceeded, a slight yellow colour appeared, together with a small amount of mercurous chloride further agitation produced a continuous deepening in colour. Th yellow colour so obtained was identical with that produced in th case of the solution which had been protected from ultra-viole light. Furthermore, on removing the solutions from the tube and allowing them to stand in the air for a short time, impur triphenylmethyl peroxide, m. p. 179°, was obtained.

The progressive generation of the characteristic yellow colou of triphenylmethyl under the above conditions affords addition confirmation of the observations made upon the specially prepare solutions of the radical. In neither case is decolorisation of th solution evident, and there is no formation of diphenylbisdipheny ene-ethane. However, a solution of triphenylmethyl of the san concentration in benzene, and prepared from the same sample the radical, when exposed to direct sunlight gave full decolorisati in less than 3 hours, together with a quantitative yield of whi crystals of diphenylbisdiphenylene-ethane.

It is to be concluded, therefore, that autoxidation and reducti of triphenylmethyl is not produced by ultra-violet radiation, a the actinic power of these rays for this particular photochemi reaction is of low order.

The Chemical Effect of the Visible Spectrum.—An experiment, which the illumination was provided by 60-c.p. electric lam in conjunction with Wratten filters of known wave-length tra mission, was not successful, and after a period of 4 weeks the cha in colour of triphenylmethyl solutions thus illuminated was imp ceptible. Furthermore, the change in colour produced in dil benzene solutions of triphenylmethyl during 4 weeks' direct expos to light from the above source was extremely slight, so that free radical can be prepared with perfect safety in a room illumina by ordinary filament electric lamps.

By employing solutions of dyes as light filters, conclusive res were obtained in direct sunlight, and the region of the visi spectrum which produced photodecomposition of triphenylmet was in this manner definitely established. The following soluti of water-soluble dyes were employed: Tartrazine (1 in 1,0 Congo-red (1 in 28,000), naphthol-green (1 in 6,000), methyl

blue (1 in 60,000), and crystal-violet (1 in 105,000). Tubes containing identical solutions of triphenylmethyl were symmetrically immersed in larger concentric tubes containing the respective dye solutions, and provision was made for the equal illumination of the systems. Exposure of the tubes to direct sunlight for 20 minutes indicated that decolorisation occurred most rapidly under green, blue, and violet light. Complete decolorisation first took place under blue illumination, whereas the solution of triphenylmethyl under red illumination was only slightly decolorised. Under yellow light, the free-radical solutions showed only slight indications of loss in colour even after several hours' exposure.

These observations indicate that the blue-green region of the spectrum is most active in effecting the photodecomposition of triphenylmethyl in benzene solution.

The Effect of the Solvent.—The nature of the solvent was found to exert a pronounced influence on the course of the photochemical reaction. As representative of non-ionising solvents we employed benzene, toluene, *m*-xylene, mesitylene, and hexane. All the solvents were carefully purified, and subjected to a final fractionation immediately before use.

2% Solutions of triphenylmethyl in each of the above solvents were introduced into the specially prepared tubes, the operations being conducted in the entire absence of air by means of the apparatus previously described. The sealed tubes were exposed at the same temperature to direct sunlight, and the respective rates of decolorisation observed by comparison with control tubes kept in the dark. Striking differences in the rates were shown by the different solutions. In toluene, decolorisation was more rapid than in benzene, in mesitylene and *m*-xylene solutions it was even faster, and in hexane most rapid of all.

Similar results were obtained when the above experiments were repeated in diffused light.

Sulphur dioxide solutions. The investigation of the behaviour of triphenylmethyl in an ionising medium naturally resolves itself into a study of the triphenylmethyl ions, either free or solvated, as distinct from that of the uncharged forms which exist in the usual non-ionising organic solvents. For our immediate purposes, sulphur dioxide appeared to be the most suitable ionising solvent. The experimental procedure differed in minor details from that adopted in the case of the preceding organic solvents, inasmuch as special provision had to be made for the preparation of standard solutions of triphenylmethyl in a low-boiling solvent of this nature.

The gas was dried by passage through a long tube containing phosphoric oxide, and was then led to the experimental tube

immersed in a freezing mixture preserved in a Dewar flask. The tube, provided with a long constriction, was previously charged with a known weight of triphenylmethyl, and after the condensation of the required volume of sulphur dioxide, the tube was sealed at the constriction by means of a blowpipe flame. 0·5% and 1% Solutions were prepared in this manner, and each solution was exposed to direct sunlight and its behaviour compared with that of a benzene solution of the same concentration. Although the benzene solution underwent rapid decolorisation in the manner previously described, no perceptible loss in colour took place in the case of the sulphur dioxide solutions.

In view of the fact that these colorimetric experiments gave no indication of photochemical autoxidation, further experiments were carried out in which the solution was exposed to sunlight in an electrolytic conductivity vessel consisting of a long tube provided with two platinum electrodes. The cell was charged with a solution of triphenylmethyl in accordance with the procedure previously indicated, and then sealed. The conductances of the solution determined at 18·5° in the dark and in sunlight showed no appreciable difference.

Action of Light on "Solid Triphenylmethyl."—The action of direct sunlight on so-called solid triphenylmethyl was investigated by sealing the finely-powdered material in thin-walled capillary tubes in an atmosphere of carbon dioxide. When exposed to sunlight for several days, the substance was found to be very slightly paler in colour, although the melting point was unchanged in comparison with samples of the same material which had throughout been protected from light. Further experiments carried out with the substance contained in tubes which were highly evacuated before sealing gave similar results.

The photochemical change in the solid state is thus of low order, and is probably due to the presence of a small amount of adsorbed solvent, since it is difficult to remove entirely the last traces of solvent even by maintaining the substance at 66° under a pressure of 15 mm.

In conclusion, we desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which partly defrayed the cost of this investigation.

UNIVERSITY COLLEGE, CARDIFF. [*Received, February 23rd, 1928.*]

CXLVII.—*A Method for the Photographic Examination of Moving Flames.*

By A. Greville White.

The method generally used for investigating flame movements is that of photographing the flame on a sensitised plate or film moving at a known speed at right angles to the direction of motion of the flame. During an examination of flame movements in tubes 2·5 cm. in diameter, it was found that direct photography of the flame in certain mixtures gave poor results, even when the lens used and the tube containing the gas mixture were both of clear quartz.

The same mixtures gave satisfactory records by the use of a method depending on the fact that the progress of a flame causes an abrupt change in the optical properties of the medium through which it passes. Light passing through the seat of the disturbance is refracted, so that if a beam passes through the tube containing the gas mixture and falls on a photographic plate moving at right angles to the direction of motion of the flame, the progress of the latter is indicated on the plate by two lines of similar form, one light and one dark. These lines are close together, and once the velocity of the plate is known, the angle between the lines on the plate and the direction of its motion gives an accurate measure of the velocity of the flame at any selected portion of the tube.

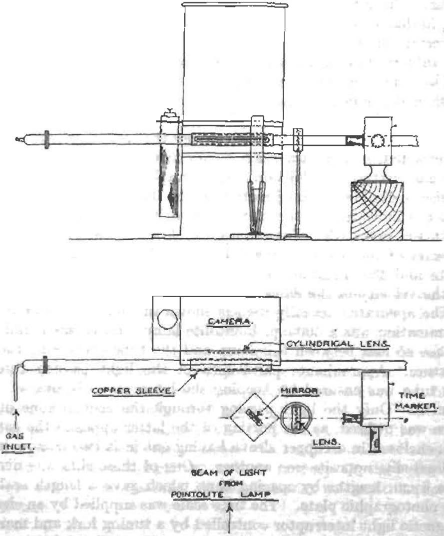
The apparatus actually used is shown in Fig. 1. The source of illumination was a 500-c.p. Pointolite lamp, and it was found best to use no lens between this lamp and the tube containing the gas mixture. Approximate parallelism of the light passing through the tube was ensured by keeping the lamp at a distance of 2 m. from it. Only the light passing through the central zone of the tube was utilised, as the portion of the latter opposite the camera was enclosed in a copper sleeve having cut in it two narrow longitudinal slits opposite one another. One of these slits was divided into 5 cm. lengths by spacing bars, which gave a length scale on the photographic plate. The time scale was supplied by an electromagnetic light interruptor controlled by a tuning fork and marking intervals of 1/100 sec. on the plate. The falling-plate camera utilised for most of the work was provided with a long cylindrical lens which focussed the light passing through the slits in the tube into a narrow band.

For the work with comparatively slowly moving flames, for which it was designed, this method has three advantages over the method of direct photography: (1) It gives better definition of the flame front, especially when it is remembered that the plates

taken show a magnification of about 1·05. (2) It gives bette resolution. By its very nature the method shows up phenomena tha would be almost, if not quite, hidden in an ordinary photograph This is well brought out by Figs. 5, 6, and 7. (3) It is independen *of the luminosity of the flame. It is thus possible to examin* hydrogen–air mixtures near the limits for the propagation o

FIG. 1.

Apparatus for the examination of moving flames.



flame, whereas direct photography gives very poor results fo mixtures containing less than 20% or more than 50% of hydrogen

Against it there could be brought one minor objection. It was necessary to synchronise the fall of the plate and the passage of the flame past the camera window. For the flames examined by the author this was easily done by hand. For much faster flames it might be necessary to ignite the flame electrically by means of a contact closed by the falling-plate holder.

Fig. 2.

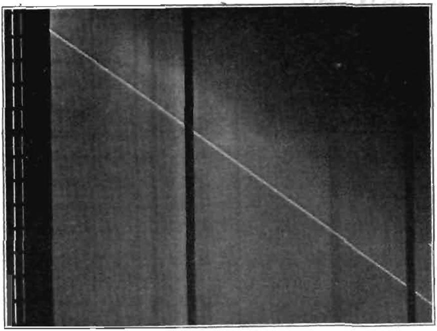
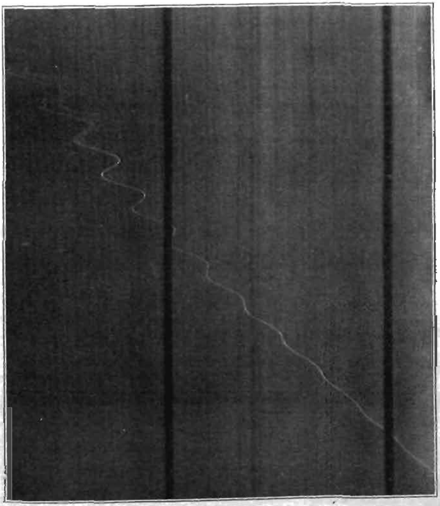


Fig. 3.



[To face p. 1160.]

Fig. 4.

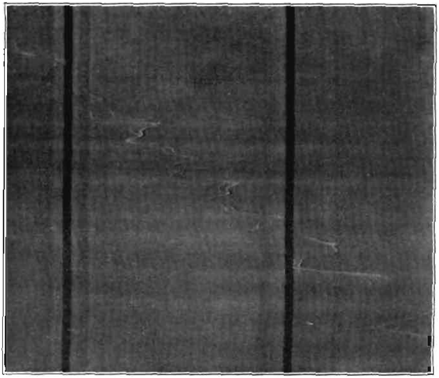


Fig. 5.

FIG. 6.

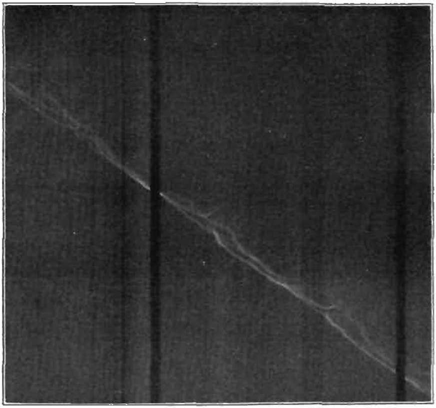
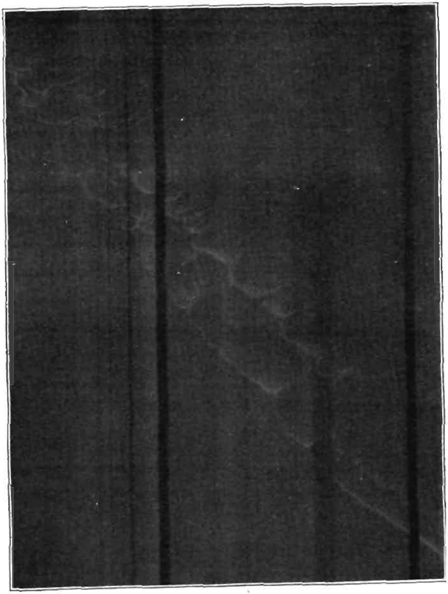


FIG. 7.



Figs. 2 to 7 show records obtained when a quiescent gas mixture was ignited by a gas flame at the open end of a horizontal, smooth, cylindrical glass tube 2·5 cm. in diameter, closed at the other end. Under these conditions, the flame generally moves at a substantially uniform speed for a certain distance, after which the motion becomes vibratory. Figs. 3 and 4 were given by mixtures in a tube 1·5 m. long; for the remainder a tube 2·98 m. long was used. All the flames are shown moving from the right to the left of the reader.

Fig. 2 shows a type of record frequently obtained for the first stage, the "uniform movement of flame." The mixture used contained 2·50% of light petroleum in air. Somewhat similar straight-line records were given by all methane- and ethane-air mixtures tested at the ordinary temperature.

Fig. 3 shows the transition from the uniform movement to the vibratory period very clearly. Vibrations at the frequency of the fundamental note of the tube increase in amplitude and suddenly give place to what may perhaps be termed the beginning of the vibratory movement proper, when the effective forward velocity of the flame is seen to decrease. This coincides with the first division of the flame trace into two parts—probably due to the production of a point of inflexion in the flame front. The mixture used contained 2·25% of light petroleum in air.

Fig. 4 shows the vibratory movement in a mixture containing 4·5% of acetylene in air, and Fig. 5 shows the uniform movement period for a mixture containing 18% of carbon disulphide in air. This record shows vibrations at the frequency of the fundamental note of the tube and illustrates the sub-division of the flame. Some of the flames left behind ultimately travel backwards. This record gave a normal value for the flame speed of this mixture. Fig. 6 shows a record given by a mixture containing 3·0% of light petroleum in air, and Fig. 7 shows that for a similar mixture containing 3·5% of light petroleum. Both records are for the "uniform movement" stage of burning. The first mixture occasionally gave flame speeds distinctly different from those normally found, and the second often did so at the ordinary temperature and gave quite erratic results when the original gas mixture was at 90°. The record shown in Fig. 6 is complex, and Fig. 7 shows that in this case we are dealing with more than one flame.

I desire to thank Imperial Chemical Industries, Ltd., and particularly Mr. Rintoul, Manager of the Research Section of Messrs. Nobel Industries, Ltd., for facilities accorded me for carrying out this work.

THE NOBEL LABORATORIES, ARDEER. [*Received, February 24th,* 1928.]

CXLVIII.—*On the Oxidation of* n-*Hexane.*

By MAX BRUNNER and ERIC KEIGHTLEY RIDEAL.

THERE is now increasing evidence that peroxides are formed during combustion of saturated hydrocarbons and play an important part in the process of detonation. A number of views have been expressed as to the nature and mechanism of their formation. According to Grün (*Ber.*, 1920, **53**, 987) a primary energy-rich "moloxide" results from the interaction of molecular oxygen with a hydrocarbon so activated as to possess a nascent double bond in which, however, the terminal carbon atom does not take part. The moloxide can under certain unspecified conditions give rise to explosion, or it can rapidly lose energy and become converted into a normal and more stable peroxide, a modification of the well-known earlier views of Traube, Manchot, and Bach.

Callendar (*Engineering*, 1927, **123**, 147, 182, 210) considers that molecular oxygen reacts directly with the hydrocarbon to form an alkyl or dialkyl peroxide, and Bennett and Mardles (J., 1927, 3155) likewise support the view that the primary product of interaction is a peroxide. On the other hand, Bone considers that combustion of these compounds involves hydroxylation rather than peroxide formation, and Lewis (J., 1927, 1555) believes that the primary reaction consists of a dehydrogenation yielding an unsaturated hydrocarbon and hydrogen; the latter is preferentially burnt, but the former might form peroxides by addition.

The autoxidation of benzaldehyde involves the primary formation of a moloxide, benzaldehyde peroxide; this in turn is converted into perbenzoic acid, which can react with benzaldehyde. It has been shown (Rideal, *Rapport du Conseil de Chimie Solvay*, 1925, p. 586; Reiff, *J. Amer. Chem. Soc.*, 1926, **48**, 2893; Brunner, *Helv. Chim. Acta*, 1927, **10**, 707) that the formation of the peroxide is primarily a surface action and that the subsequent reactions of the peroxide can continue in the homogeneous phase. The investigations of Bäckstrom (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927 *J. Amer. Chem. Soc.*, 1927, **49**, 1460), however, led him to the conclusion that the oxidation of benzaldehyde was an example of the chain mechanism of the type first postulated by Christiansen and Kramers (*J. Physical Chem.*, 1924, **28**, 145). It was suggested by one of us (E. K. R.) that the discrepancy between the two conclusions could be reconciled on the assumption that chain reactions only commence in these autoxidative processes when the *peroxide* concentration, produced initially at surfaces, rises to certain critical values. In support of this view, it was urged that, in the

autoxidation of benzaldehyde with relatively inactive or poisoned catalysts, a period of induction is always observed. During this period of induction the peroxide content of the solution gradually rises, and almost abruptly the reaction acquires an enormous increase in velocity. It is possible that the cause of chain formation when the peroxide concentration has risen to a critical value is purely thermal (the temperature coefficient is about 2·4 for a rise of 10°), but several arguments can be advanced in favour of the alternative view of a true chain of excitation by collision between *peroxide* molecules.

In this paper the behaviour of hexane is compared and contrasted with that of benzaldehyde. Owing to the return of one of us (M. B.) to Switzerland, the comparison has not been pursued in detail, but some of the results obtained differ so markedly from those of other investigators that it was thought desirable to place them on record.

It seemed probable that the process of oxidation of hexane would be similar to that of benzaldehyde, *viz.*, one of autoxidation involving the primary formation of a moloxide by addition of molecular oxygen, which is probably a surface action, followed by a conversion of the moloxide into a peroxide which can react with hexane either in the gas phase or at surfaces. When, however, the concentration of the peroxide in the gas phase rises to certain critical values, this gives rise to a chain mechanism for combustion. According to the experiments of Callendar (*loc. cit.*), the normal saturated hydrocarbons possess characteristic temperatures of initial combustion (T.I.C.), the value of which is, however, affected by the composition of the gas mixture. Callendar finds the T.I.C. for hexane to be 205° in a 33% hexane–air mixture, rising to 390° in a 1·9% mixture. Lewis noted similar critical temperatures, that for hexane being at 232°; he termed these "critical inflexion temperatures" (C.I.T.). He also stated that the value was somewhat affected by the size of the vessel or the presence of platinum; that rapid heating gave a less steep inflexion in the pressure–temperature curves; that a large proportion of hexane lowered the C.I.T. as well as the T.I.C. (Callendar); and finally, that the presence of a small quantity of water was necessary, as in the case of the autoxidation of benzaldehyde (*loc. cit.*).

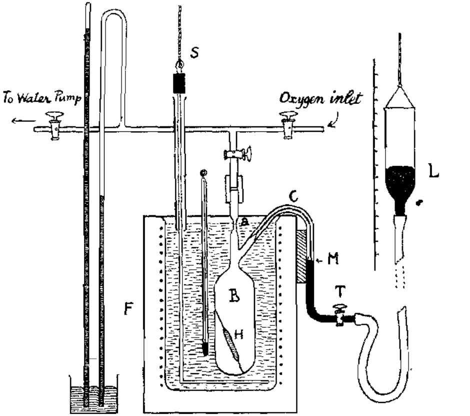
Repetition of these experiments under various conditions led us to the conclusion that hexane possessed no such critical temperature, and that before a period of rapid combustion takes place at any temperature it is necessary to keep the hexane–air mixture at that temperature for a certain period of time; in fact, the autoxidation process of hexane is similar to that of benzaldehyde,

in that there is an apparent period of induction, which is capable of variation. *During this period of induction, which is affected* by temperature, peroxide formation, decomposition, and reaction with hexane likewise occur, the peroxide content rising until the period of rapid combustion commences. The period of induction is also affected by inhibitors, such as aniline, as well as by surface catalysts like pumice.

EXPERIMENTAL.

n-Hexane was purified by repeated treatment with concentrated sulphuric acid, 20% oleum, and caustic soda, the fraction distilling

FIG. 1.



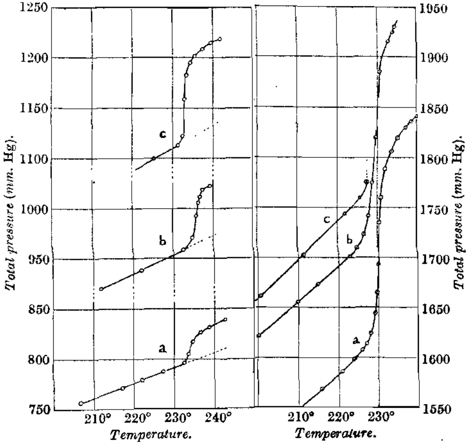
from sodium at 68·99—69·06° (corr.) being employed. Oxygen from a cylinder was dried over phosphoric anhydride and purified from carbon dioxide.

The reaction vessel (Fig. 1) consisted of a Pyrex bulb, *B*, connected by capillary tube, *C*, to the mercury manometer, *L*. A small sealed bulb, *H*, *containing a known weight of hexane*, was introduced and the bulb, *B*, was evacuated, filled with oxygen to the desired pressure, and sealed off at *a*. The small bulb, *H*, was broken by agitation, and the reaction vessel then placed in an electrically heated and well-stirred oil-bath, *F*. The mercury level

in *L* was maintained at a definite mark, *M*, in the capillary tube close to its entrance to the reaction vessel.

Condensation of hexane in the capillary was readily prevented by occasional warming. The temperature of the oil-bath could be maintained by electrical relay to within 0·1°. At the completion of the reaction, the vessel *B* was removed from the oil-bath, cooled in a mixture of ice and salt, and the final pressure determined at a definite temperature. The reaction vessel was connected to a

FIG. 2. FIG. 3.

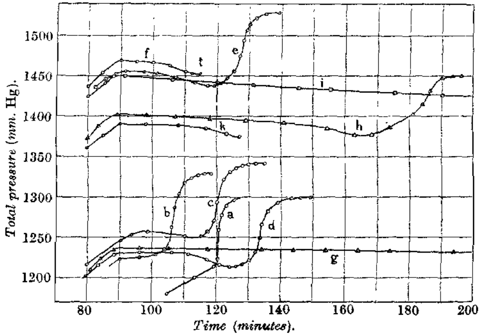


mercury-filled gas burette, and a fraction of the gas drawn into the burette. The gas analysis comprised determinations of oxygen, carbon dioxide and monoxide, and unsaturated hydrocarbons, and in a few cases the residual gas was analysed by combustion over copper oxide in a quartz capillary. Before each experiment the vessel *B* was thoroughly cleaned with hot chromic acid, washed with water, and dried.

In Figs. 2 and 3 are shown the results obtained on heating hexane–oxygen mixtures in the manner described; the apparent C.I.T. is noted at 232°. With increasing proportion of oxygen there is likewise an increase in the total pressure after the period of rapid

combustion has taken place (*i.e.*, at the apparent C.I.T.), and from the following table it will be seen that this increase is almost proportional to the oxygen content of the gas until the hexane content has fallen to 31·7% (Fig. 3, *c*), where the reaction becomes explosive, chemiluminescence occurs, and large quantities of soot are deposited. Owing to the explosive nature of this reaction, the analytical figures are only approximate, but the quantities of unsaturated hydrocarbons formed (which resembled isoprene in odour) show a marked increase with increasing pressure. It is significant that the transition from the small increase of pressures observed with hexane-rich mixtures to the explosive mixture (*ca.* $C_6H_{14} + 2O_2$) is gradual,

Fig. 4.



both the temperature and the initial slope of the pressure curve being identical (see Fig. 3, *b* and *c*).

Curve.	Hexane, % by vol.	% Increase in pressure at the C.I.T. (= *b*).	% O_2 / *b*	Gas analysis, %. CO_2.	Unsaturated hydrocarbons.	CO.	O_2.
Fig. 2, *a*	77·9	3·39	6·5				
b	63·3	5·53	6·6				
c	50·8	7·28	6·7	28·04	0·23	27·73	
Fig. 3, *a*	35·7	12·0	5·3				
b	33·7	11·7	5·7	38·04	1·13	29·76	0·36
c	31·7	Explosion		7·01	3·61	26·65	2·5

In Fig. 4 are shown the curves obtained on heating hexane oxygen mixtures to definite temperatures and maintaining the

at these temperatures until the sudden pressure increase was noted. The experimental conditions and results were as follows :

Curve.	Hexane, % by vol.	Final temp. of oil-bath.	Apparent period of induction (mins.).	Remarks.
a	50·8	232°	Nil	Experimental conditions as realised by Lewis and in the former series.
b	45·7	220	7	
c	45·2	215	17	
d	46·1	210	37	Final pressure increase = 86 mm.
e	43·8	210	30	Showing the influence of pressure on shortening the period of induction.
f	43·9	210	—	Stopped for analysis at *t*, see curve.
g	46·0	210	232	With 2·0 mg. of aniline; final pressure increase only 31 mm.
h	44·0	210	76	With 0·25—0·3 mg. aniline; final pressure increase = 73 mm.

The existence of a period of induction is clearly observed. Although in all cases the initial heating of the oil-bath to the desired temperature occupied some 90 minutes, the error introduced by this procedure must be small, since, owing to the apparently large temperature coefficient of the reaction shortening the period of induction, this period would probably be of the order of 100 minutes at 200°. In Curve *a* the induction period is telescoped into the period of initial combustion, as in the experiments of Lewis and those described in the previous section. The induction period is also shortened by an increase in the total pressure of the reactants, *e.g.*, in experiments *d* and *e* the induction period has been reduced from 37 to 30 mins., *i.e.*, in the ratio of 1·23 to 1, by an increase in the total pressure from 1230 mm. to 1450 mm. with hexane contents of 43·8% and 46·1%, respectively; the oxygen pressures thus stand in the ratio of 815 to 664 mm., *i.e.*, 1·22 to 1. The rate of the reaction which governs the induction period is thus determined by the oxygen pressure over these ranges of pressure and temperature.

This period of induction is very similar to that observed in the autoxidation of benzaldehyde, in that it is sensitive to temperature changes and greatly affected by small quantities of inhibitors (*g*, *h*). For instance, 0·25 mg. of aniline (*h*) produces an induction period of 76 mins. for the reaction at 210°, whereas in the autoxidation of benzaldehyde at 20°, 0·20 mg. of iodine produces an induction period of 40 mins. (Brunner, *loc. cit.*, p. 722). With 2·0 mg. of aniline under the same conditions (*g*) the induction period is lengthened to 232 mins. At the end of this period the rapid reaction set in, but this proceeded more slowly, taking 70 mins. and giving a pressure increase of only 31 mm. Without any inhibitor the

induction period is 37 mins., the main reaction taking 21 mins., with a pressure increase of 86 mm.

It seemed probable that during the period of induction the formation of a hexane moloxide, and thus of a peroxide, was taking place in a manner analogous to the benzaldehyde reaction. It is noted that during the period of induction at constant temperature there is always a small but definite fall in pressure, usually some 15 mm. Whilst the formation of the moloxide and of the peroxide would be accompanied by a fall in pressure, the possibility of the formation of polymerised products of unsaturated hydrocarbons, or of non-volatile oxidation products, renders the observation less significant. An analysis was accordingly carried out on a mixture just before the increase in pressure had commenced. At the point corresponding to t (Curve f), the bulb was removed, cooled to 0° in ice, and opened under an acid solution of potassium iodide; after thorough agitation the peroxide was determined by titration of the liberated iodine with $N/100$-sodium thiosulphate. The original weight of hexane was 0·101 g. with an oxygen pressure of 400 mm. at 14·3° in a bulb of 57·6 c.c.; the weight of peroxide obtained, calculated on the formula $C_6H_{14}O_2$, was 0·0032 g., or nearly 3·2% of the original hexane. That this figure does not represent the total formation of peroxide during the period of induction, but that some peroxide had already reacted with hexane to produce oxidation products, was confirmed by another analysis on a 44·3% hexane mixture after a period of induction of 35 mins. at 210° (Curve k). The analysis showed 13·02% CO_2, 1·23% unsaturated compounds, 68·1% O_2, and 6·8% CO, and the gas also contained some 3% of nitrogen from the original oxygen and a small quantity of hydrogen and hydrocarbon vapour. It is clear that at least 30% of the original oxygen had been consumed during this period of induction. At the moment of the commencement of the period of rapid combustion there is 0·0032 g. of peroxide present in the vessel, which is equivalent to a gas pressure of 14·17 mm. at 210°. Taking the molecular weight of the peroxide as 118 and the molecular radius as 5×10^{-8} cm., we obtain for the mean time interval between collisions of peroxide molecules a value of $1{\cdot}10 \times 10^{-8}$ sec., which is comparable with that obtained for excited molecules. Such a period is therefore in agreement with the conception of a chain mechanism of excitation of peroxide molecules.

If the active surface in a process of autoxidation be increased in the case of benzaldehyde oxidation two effects are to be observed (1) Certain catalysts, such as glass powder and pumice, increase

the rate of peroxide formation; these shorten the period of induction and increase the rate of maximum oxygen uptake. (2) Others, like charcoal, catalytically destroy the peroxide and thus decrease the rate of oxidation.

With powdered pumice (1 g.) present in a 43·8% hexane–oxygen mixture at 210°, Curve *i* was obtained. Even after 325 mins. there was no period of rapid oxidation, although a total pressure fall of 57 mm. was observed. At the end of this period analysis of the gas revealed the pressure of 57·19% CO_2, 0·69% unsaturated compounds, 13·56% O_2, and 16·3% CO. It is clear that combustion is taking place but at a slow rate—a phenomenon similar to that observed with charcoal in the autoxidation of benzaldehyde.

Furthermore, it is clear that the slow combustion differs from the rapid in that there is not an increase but a slight decrease in pressure —an indication that aldehydes and acids as well as polymerised products are formed in quantities sufficient to nullify any increase in pressure caused by the interaction of the hexane peroxide with hexane to produce carbon dioxide and water. It seems probable that during this period of slow reaction a number of chemical reactions involving peroxide molecules are taking place, and the identification of small quantities of products isolated affords some slight experimental evidence for the following:

(1) Decomposition to aldehyde and water, followed by partial further oxidation and condensation of the aldehyde produced.

(2) Reaction with hexane to produce unsaturated hydrocarbon and water. The unsaturated hydrocarbons produced undergo polymerisation or further oxidation.

During the period of rapid combustion, the chain-excited peroxide molecules react and act as centres of activation for normal hexane molecules, which then undergo direct combustion. The importance of peroxides in these secondary reactions has been emphasised by Egerton (*Nature*, 1928, **121**, 10).

The necessity for the preliminary formation of a high concentration of reaction centres for the propagation of a chain reaction does not appear to be confined to oxidation of benzaldehyde and saturated hydrocarbons, for similar conclusions can be drawn from the observations of Chariton and Walta (*Z. Physik*, 1926, **39**, 547) on the oxidation of phosphorus vapour, and from the numerous interactions between the alkali metals and substances such as pentachloroethane and bromoform (Staudinger, *Z. angew. Chem.*, 1925, **38**, 578).

Summary.

The process of oxidation of *n*-hexane has been shown to bear a striking similarity to the autoxidation of benzaldehyde. The temperature of initial combustion has been shown not to be a characteristic of the hydrocarbon, for rapid combustion will set in after a period of induction at lower temperatures. During this period of induction slow autoxidation proceeds together with the formation of peroxides. The period of induction at constant temperature is greatly affected by the oxygen pressure and by the presence of inhibitors, such as aniline, or of surface catalysts, such as pumice. The temperature coefficients of the reactions proceeding in the induction period are high.

The suggestion is made that the reactions involve the formation at catalytic surfaces of an active moloxide, which is subsequently converted into a more stable peroxide. The peroxide can react either in the gas phase or at the surface, but when the peroxide concentration reaches a critical value, chain propagation ensues, causing excitation and combustion of molecules coming into contact with the reaction centres of the chain.

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CXLIX.—*The Isomerism of the Styryl Alkyl Ketones. Part IV. 4-Hydroxy- and Some Derivatives of 2-Hydroxy-styryl Alkyl Ketones.*

By ALEXANDER McGOOKIN and DONALD JAMES SINCLAIR.

THE examination of a further series of styryl alkyl ketones has led to some interesting developments and to a confirmation of the earlier work (J., 1924, **125**, 2099; 1925, **127**, 2539; 1926, 1578).

5-Bromo-2-hydroxystyryl methyl ketone (Part I) reacts in alkaline solution like the 2-hydroxy-compound with the production of the sodium salt of the distyryl ketone. In addition to the yellow distyryl ketone described by Fabinyi and Széki (*Ber.*, 1907, **40**, 3455), a colourless *isomeride* of different m. p. has now been prepared. Instances of isomerism amongst the distyryl ketones are rare, although this type of ketone could exist in three isomeric forms.

Zincke and Muhlhausen (*Ber.*, 1903, **36**, 129) and Vorländer (*Ber.*, 1925, **58**, 118) obtained green and yellow forms of 4 : 4′-dihydroxydistyryl ketone. Straus (*Annalen*, 1910, **374**, 40) described

yellow and colourless modifications of 4 : 4′-dimethoxydistyryl ketone of different m. p.'s. Heilbron and Whitworth (J., **1923**, **123**, 238) prepared 4′-dimethylamino-2-hydroxy-3-methoxydistyryl ketone in two red forms having differing m. p.'s. Dickinson, Heilbron, and Irving (J., 1927, 1888) isolated 3 : 3′-dimethoxy-4 : 4′-dibenzyloxydistyryl ketone and an isomeride of different m. p. Glaser and Tramer (*J. pr. Chem.*, 1927, **116**, 331) described a green form of 2 : 2′-dihydroxydistyryl ketone obtained by heating the ordinary yellow isomeride. The present authors were able to isolate only a green, impure specimen of diphenos*piro*pyran by this treatment (Part I). Glaser and Tramer (*loc. cit.*) also prepared a green form of 4 : 4′-dihydroxy-3 : 3′-dimethoxydistyryl ketone which must be an isomeride of the compound described in Part III and by Nomura and Hotta (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 119). Glaser and Tramer also discuss the fission occurring in the molecules of unsaturated ketones which has already been considered in the present series.

2-Hydroxy-4-methoxystyryl ethyl ketone, *2-hydroxy-4-methoxystyryl* n-*propyl ketone*, *2-hydroxy-3-methoxystyryl ethyl ketone*, *2-hydroxy-3-methoxystyryl* n-*propyl ketone*, *4-hydroxystyryl methyl ketone*, *4-hydroxystyryl ethyl ketone*, and *2-hydroxystyryl* iso*propyl ketone* were found to be similar to the ketones previously described.

Nomura and Nozawa (*Sci. Rep. Tôhoku Imp. Univ.*, 1918, **7**, 79) described the preparation of 3-hydroxystyryl methyl ketone by the direct method. Attempts to repeat the condensation both in acid and in alkaline media resulted in the production of a buff-coloured, amorphous solid, possibly a polymeride of the simple ketone, into which it could not be converted. The simple ketone was prepared by the method of Murai (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 149) from 3-nitrostyryl methyl ketone, which the present authors found to melt at a temperature higher than that recorded by Murai (*loc. cit.*) and by Vorländer (*Annalen*, 1897, **294**, 273). Attempts to isolate the 3-amino-compound previously prepared by Miller and Rhode (*Ber.*, 1890, **23**, 1881), as an oil, were unsuccessful.

No distyryl ketone is produced by the action of alkali on 4-hydroxystyryl methyl ketone, and this compound will not condense with 4-hydroxybenzaldehyde in alkaline media, previous observations on the failure of 4-hydroxybenzaldehydes to condense under these conditions (Part I) or to react only to a very slight extent (Part II) thus being confirmed. 4 : 4′-Dihydroxydistyryl ketone has been prepared only by acid condensation (compare Zincke and Muhlhausen, *loc. cit.*; Vorländer, *loc. cit.*).

Attempts to prepare 2-hydroxystyryl benzhydryl ketone by the

direct condensation of salicylaldehyde and benzhydryl methyl ketone in presence of 40% potassium hydroxide solution, sodium ethoxide or piperidine were unsuccessful, although benzhydryl methyl ketone has been condensed with benzaldehyde and its 4-methoxy-derivative by Rack (*Ber.*, 1923, **56**, 1130).

In order to prove that aldehydes do not react with the methylene groups of ketones in the presence of alkalis, attempts were made to condense salicylaldehyde with diethyl ketone and with 2-hydroxystyryl ethyl ketone under these conditions without success. Even the reactive 4-dimethylaminobenzaldehyde would not condense with 2-hydroxystyryl ethyl ketone in alkaline media.

The hydroxystyryl alkyl ketones so far described are of two types. The ketones of both types undergo fission in alkaline media, furnish red solutions more or less readily when boiled with concentrated hydrochloric acid, and exist each in isomeric forms of identical m. p. The ketones of type I all contain the group $>CH{:}CH{\cdot}CO{\cdot}CH_3$ and their fission products recombine in alkaline solution to form the distyryl ketones. The ketones of type II contain the group $>CH{:}CH{\cdot}CO{\cdot}CH_2R$, where R is any alkyl group, and their fission products recombine in alkaline media with the formation of high-melting, unsaturated substances of undetermined nature.

Styryl ketones of a third type have now been prepared which differ from those of types I and II in that (i) alkali has no action, other than solvent action, upon them even on prolonged exposure, and (ii) they are not attacked by boiling concentrated hydrochloric acid.

2-Hydroxystyryl tert.*-butyl ketone, 2-hydroxystyryl phenyl ketone,* and *2-hydroxystyryl* iso*butenyl ketone* belong to this class. The second of these compounds has not been isomerised, but the other two exist in the usual isomeric forms.

2-Hydroxystyryl *iso*butenyl ketone (I) is formed in small yield by the condensation of salicylaldehyde with mesityl oxide in alkaline solution, the main products being 2-hydroxystyryl methyl ketone and 2 : 2′-dihydroxydistyryl ketone, which are formed thus (X denotes $HO{\cdot}C_6H_4$) :

$$\text{(I.)}\quad X{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CMe_2 \xrightarrow{H_2O} X{\cdot}CH{:}CH{\cdot}COMe + COMe_2.$$

$$2X{\cdot}CHO + Me_2CO = (X{\cdot}CH{:}CH)_2CO + 2H_2O.$$

Other instances of isomerism amongst the styryl ketones (see table) appear in the literature, although they have not previously been recognised. In addition a number of styryl aryl ketones are known, the isomeric forms having different m. p.'s ; data regarding these compounds will be published elsewhere.

Ketone.	M. p. of forms. Yellow.	Colourless.	Reference.
4-Methoxystyryl methyl	—	73°	Einhorn and Grabfeld, *Ann.*, 1888, **243**, 362.
	—	72—74	Baeyer and Villiger, *Ber.*, 1902, **35**, 1189.
	74—75°	—	Nomura and Nozawa, *loc. cit.*
3-Nitro-4-methoxystyryl methyl	159	159(?)	Einhorn and Grabfeld, *loc. cit.*
2-Methoxystyryl methyl	—	48—50	Auwers, *Ann.*, 1917, **413**, 279.
	50	—	Heilbron and Buck, *J.*, 1921, **119**, 1500.
	50	—	Faillebin, *Ann. Chim.*, 1925, **4**, 410.
3-Methoxy-4-ethoxystyryl methyl	106	106	Dickinson, Heilbron, and Irving, J., 1927, 1888.
3-Nitrostyryl phenyl	145—146	—	Sorge, *Ber.*, 1902, **35**, 1065.
	146	—	Ruhemann, J., 1903, **83**, 1371.
	—	143—144	Bodforss, *Ber.*, 1916, **49**, 2795.
2-Methoxystyryl phenyl	58—59	—	Stobbe and Wilson, J., 1910, **97**, 1732.
	—	60	Forster and Heilbron, J., 1924, **125**, 340.
4-Methoxystyryl phenyl	107	—	Pfeiffer, *Ann.*, 1917, **412**, 253.
	—	106—107	Stockhausen and Gattermann, *Ber.*, 1892, **25**, 3535.
4-Aldehydostyryl phenyl	125	125(?)	Lendenfeld, *Monatsh.*, 1906, **27**, 169.
4-Methoxy-β-phenylstyryl phenyl	113	—	Klages and Tetzner, *Ber.*, 1902, **35**, 3965.
	—	113	Das and Ghosh, J., 1919, **115**, 817.

Experimental.

5 : 5'-*Dibromo*-2 : 2'-*dihydroxydistyryl Ketone*.—The sodium salt slowly separated in green crystals from the red solution produced by treatment of the monostyryl methyl ketone with alkali. Acidification of a solution of these crystals produced the free ketone, which separated from alcohol in bright yellow crystals, m. p. 188°. It can also be prepared by the usual condensation methods (i) from 5-bromo-2-hydroxystyryl methyl ketone and 5-bromosalicylaldehyde, and (ii) from 5-bromosalicylaldehyde and acetone. A solution of the aldehyde (50 g.) in 10% aqueous sodium hydroxide (150 c.c.) was diluted with 700 c.c. of water, and acetone (7·2 g.) introduced. After 4 days, the green crystals that had separated were collected, dissolved in water, and almost neutralised with dilute acetic acid, and the ketone was precipitated with carbon dioxide. Recrystallisation from benzene produced yellow, matted crystals, m. p. 188°. The mother-liquor furnished a greyish solid which, after recrystallisation, separated in colourless, rhombic crystals, m. p. 174·5° (Found : C, 48·3 ; H, 2·95 ; Br, 37·95. $C_{17}H_{12}O_3Br_2$ requires C, 48·1 ; H, 2·8 ; Br, 37·7%). This compound dissolved in alkali with a yellow colour, being thus distinguished readily from the yellow isomeride. A mixture of the two forms melted at 174·5°.

Many of the styryl ketones described below were obtained by the following alkali-condensation method. A solution of the aldehyde and the ketone in alcohol (80—150 c.c.) was treated with 20% sodium hydroxide solution and after a time (12 hours—3 days) an aqueous solution of the crystals that had separated, or the

original liquid if no crystals separated, was acidified; the styryl ketone obtained was crystallised from alcohol or benzene.

2-*Hydroxy*-4-*methoxystyryl ethyl ketone*, obtained from 2-hydroxy-4-methoxybenzaldehyde (10 g.), methyl ethyl ketone (5 g.), and alkali (250 c.c.), formed yellow crystals, m. p. 123°, which rapidly became green when kept. Recrystallisation then yielded colourless needles, m. p. 123° (Found : C, 69·4; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). The colourless form dissolved in alkali, giving a yellow solution which turned orange in 5 days.

2-*Hydroxy*-4-*methoxystyryl propyl ketone*, obtained from 2-hydroxy-4-methoxybenzaldehyde (9 g.), methyl *n*-propyl ketone (20 g.), and alkali (150 c.c.), formed yellow needles, m. p. 111—112°. The colourless form, obtained in the usual way, melted at 111—112° and gave a yellow alkaline solution which developed an orange tint after 8 days (Found : C, 70·9; H, 7·35. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

2-*Hydroxy*-3-*methoxystyryl ethyl ketone*, prepared from 2-hydroxy-3-methoxybenzaldehyde (20 g.), methyl ethyl ketone (9·5 g.), and alkali (25 g. KOH in 155 c.c. water), was obtained as a hydrate in pale yellow needles, m. p. 77—79°, which could be dehydrated only by heating in a steam-oven. The product crystallised from benzene–hexane in colourless needles, m. p. 86·5°, the solution of which in alkali was orange-coloured (Found : C, 69·5; H, 6·8. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

2-*Hydroxy*-3-*methoxystyryl propyl ketone*, obtained from 2-hydroxy-3-methoxybenzaldehyde (10 g.), methyl *n*-propyl ketone (5 g.), and alkali (400 c.c.), formed colourless, arrow-shaped crystals (from alcohol), m. p. 82·5°, giving an orange solution in alkali (Found : C, 70·9; H, 7·1. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

3-*Hydroxystyryl Methyl Ketone*.—(i) In an attempt to prepare this ketone from 3-hydroxybenzaldehyde (12 g.), acetone (5 c.c.), and alkali (100 c.c. of 20% KOH), a dark brown, amorphous substance was obtained which, on solution in methyl alcohol and fractional precipitation with water, gave a buff-coloured solid which resisted all attempts at further purification and decomposed at a high temperature without melting. Vacuum distillation of 20 g. of the solid only yielded a few c.c. of a dark, uncrystallisable oil with a phenolic odour.

(ii) 3-Hydroxybenzaldehyde (13 g.) in acetone (30 c.c.) was cooled in ice, and dry hydrogen chloride passed in; a dark violet solid then separated. The product contained chlorine but was easily freed from hydrochloric acid by water, with the formation of the amorphous solid already described.

(iii) The method of Murai (*loc. cit.*) was followed. The 3-nitro-

styryl methyl ketone obtained as an intermediate was a pale yellow solid of m. p. 99—100° (Found: N, 7·45. Calc. for $C_{10}H_9O_3N$ · N, 7·3%). The 3-hydroxystyryl methyl ketone consisted of faintly coloured crystals of m. p. 97—98°. Its yellow solution in alkali slowly turned orange.

4-*Hydroxystyryl methyl ketone*, obtained from 4-hydroxybenzaldehyde (25 g.), acetone (12 g.), and alkali (250 c.c.), formed yellow needles, m. p. 52—62°, containing water which was removed by crystallisation from absolute alcohol, pale lemon-yellow crystals, m. p. 111—112°, then separating. The colourless isomeride of identical m. p. could be prepared by the usual methods or by the addition of 40% alkali to the condensation mixture; in the latter case the sodium salt separated in deep yellow needles [Found: (yellow isomeride) C, 73·8; H, 6·2; (colourless isomeride) C, 73·6; H, 6·2. $C_{10}H_{10}O_2$ requires C, 74·0; H, 6·2%].

The mother-liquor from the preparation of 4-hydroxystyryl methyl ketone contained a small quantity of a yellow, crystalline compound, m. p. 220° (Found: C, 75·8, 76·0; H, 5·2, 5·2%), the constitution of which has not been determined.

4 : 4′-*Dihydroxydistyryl Ketone.*—Dry hydrogen chloride was passed into a solution of 4-hydroxybenzaldehyde (25 g.) and acetone (6 g.) in absolute alcohol (100 c.c.); a blackish solid soon separated which turned green on the addition of water. Crystallisation from alcohol then yielded yellow plates, m. p. 237—238°. Acid condensation of 4-hydroxybenzaldehyde and 4-hydroxystyryl methyl ketone gave the same compound.

4-*Hydroxystyryl ethyl ketone* was obtained from 4-hydroxybenzaldehyde (25 g.), methyl ethyl ketone (15 g.), and alkali (300 c.c. of 15%; warming on the water-bath) as a yellow oil which crystallised in the ice-chest; it then separated from cold aqueous alcohol in yellow needles and from hot alcohol in colourless needles (Found: C, 74·6; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%), both having m. p. 115°.

4-*Hydroxystyryl propyl ketone*, obtained from 4-hydroxybenzaldehyde (25 g.), methyl *n*-propyl ketone (15 g.), and alkali (200 c.c.), separated from cold aqueous alcohol in yellow crystals, m. p. 80—83°, of a hydrate which, on recrystallisation from benzene–hexane, gave yellow needles, m. p. 90°. The colourless isomeride of the same m. p. was produced in the usual way [Found: (yellow form) C, 75·5; H, 7·45; (colourless form) C, 75·3; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%].

2-*Hydroxystyryl* iso*propyl ketone*, obtained from methyl *iso*propyl ketone (50 g.), salicylaldehyde (72 g.) and alkali (700 c.c.), separated from ice-cold alcohol in yellow crystals, m. p. 107°. This form was

very unstable and passed readily into the colourless modification, m. p. 107° (Found: C, 75·9; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

2-*Hydroxystyryl* tert.-*Butyl Ketone*.—A solution of pinacolin (18 g.), salicylaldehyde (18 g.), and sodium hydroxide (10 g.) in alcohol (200 c.c.) was warmed on a water-bath for ½ hour. After 7 days, the excess of pinacolin was removed by evaporation (otherwise an uncrystallisable oil separated on acidification), and the solution was diluted with water and poured into dilute acetic acid. Crystallisation of the product from cold aqueous alcohol gave yellow needles, m. p. 128°, which were easily converted into the colourless form of identical m. p. (Found: C, 76·0; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·8%). Both forms give yellow solutions in alkali.

2-*Hydroxystyryl* iso*Butenyl Ketone* (I).—Salicylaldehyde (38 g.) was dissolved in alcohol (100 c.c.), and 20% sodium hydroxide solution (200 c.c.) added. Pure mesityl oxide (30 g.) was gradually run in with mechanical stirring. After 12 hours, the dark red sodium salt produced was filtered off and treated with water; a small amount of material remaining undissolved was found to be the required *ketone*, which, on recrystallisation, yielded yellow crystals, m. p. 141°. On acidification, the sodium salt furnished 2 : 2′-dihydroxydistyryl ketone, and the original filtrate gave 2-hydroxystyryl methyl ketone. A colourless *isomeride*, m. p. 141°, of 2-hydroxystyryl *iso*butenyl ketone was prepared by the usual methods. The pure ketone dissolved in concentrated alkali solution with a yellow colour which was unchanged on standing, but after the addition of salicylaldehyde the solution turned red in 2 hours and longer treatment caused the separation of the sodium salt of 2 : 2′-dihydroxydistyryl ketone. No coloration was produced when 2-hydroxystyryl *iso*butenyl ketone was boiled with concentrated hydrochloric acid (Found: C, 76·9; H, 7·0. $C_{13}H_{16}O_4$ requires C, 77·2; H, 6·9%).

2-*Hydroxystyryl Phenyl Ketone*.—This ketone was prepared by a modification of Bablich and Kostanecki's method (*Ber.*, 1896, **29**, 233). It gives an orange-red sodium salt, and an orange solution in alkali. An alcoholic solution of the sodium salt was made by dissolving the ketone in the exact amount of standard sodium ethoxide solution, and six fractions were obtained by successive additions of dry ether. All the sodium salts thus precipitated and also the salt obtained on evaporation of the final filtrate gave 2-hydroxystyryl phenyl ketone on acidification. Boiling in high-boiling solvents in presence of acids, exposure to ultra-violet light, and heating in an autoclave failed to isomerise this ketone, the yellow form being recovered in every case.

During the preparation of this ketone red needles separated from the reaction mixture. Treatment of these crystals with water caused the precipitation of a small amount of a yellow solid which proved to be 2-hydroxybenzylidenediacetophenone. When pure and of constant melting point, it consisted of colourless plates of m. p. 129°, which is lower by 2° than that recorded. The compound *is insoluble in alkali of less than 15% strength, but dissolves in* more concentrated alkali, yielding yellow solutions.

The authors desire to express their thanks to Dr. Dickinson for an analysis, to Mr. G. E. Follows, M.Sc., for observing the colourless isomeride of 5 : 5′-dibromo-2 : 2′-dihydroxydistyryl ketone, and to Mr. C. F. A. Roberts for the preparation of 3-hydroxystyryl methyl ketone.

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CL.—*Some Miscibility Relations of Acetic Anhydride.*

By DAVID CHARLES JONES and HAROLD FREDERICK BETTS.

ORTON and JONES (J., 1912, **101**, 1722) determined the solubility of water in acetic anhydride at 15°, and Lumière and Barbier (*Bull. Soc. chim.*, 1905, **33**, 783) state that acetic anhydride is soluble in water to the extent of 12% at the ordinary temperature. No other data regarding the mutual solubility of acetic anhydride and any other liquid are given in the literature.

The solubility of pure acetic anhydride in carbon disulphide, *cyclo*hexane, and a petroleum fraction has now been determined, and found to be much less in each solvent than that of acetic acid itself (see Jones, J., 1923, **123**, 1374). The effect of acetic acid, present as an impurity in the anhydride, on the critical solution temperatures (C.S.T.) has also been investigated.

At first sight it seemed very remarkable that the stable compound formed by chemical union between two acetic acid molecules with the elimination of *water* should prove to be less soluble in these solvents than the associated acid. The much greater solubility of acetic acid than of its anhydride in water is roughly what would be expected from C_2 and C_4 compounds and their respective water-soluble groups. With petroleum as solvent, since we are dealing with the associated acid, in both cases we have C_4 compounds, and a greater similarity in the solubility would be expected, *i.e.*, the solubility of the anhydride would be relatively increased. The *greater* solubility of the associated acid in petroleum must then be ascribed to its smaller polarity. In the process of association, the

highly polar carboxyl groups, which are active in promoting solubility in water, are conjugated in such a way that the resulting compound is less polar than its anhydride. All the known facts concerning the physical properties of the (pure, associated) acid are in agreement with this conclusion; *e.g.*, acetic acid, $\epsilon_{19^{\circ}} = 6{\cdot}29$, $\gamma_{20^{\circ}} = 27{\cdot}90$; acetic anhydride, $\epsilon_{20^{\circ}} = 20{\cdot}5$, $\gamma_{20^{\circ}} = 32{\cdot}69$ (ϵ = dielectric constant; γ = surface tension). It follows that, if its true solubility could be determined, pure, associated acetic acid should be much less soluble in water than the anhydride.

Acetic anhydride, although it has a fairly high dielectric constant, is a typical non-associated liquid if examined by all the usual criteria. Its mutual solubility with solvents of the petroleum type affords a rare example of partial miscibility of liquids neither of which is associated. A calculation of the internal pressure of the anhydride by some of the usual methods leads to values which place it somewhere near benzene in the internal-pressure series; and therefore, according to the theories of solubility put forward by Hildebrand and his collaborators, acetic anhydride should prove completely miscible in these solvents.

E X P E R I M E N T A L.

Purification of Materials.—Acetic anhydride. For the purification of this material the method used by Orton and Jones (*loc. cit.*) was found very effective. Kahlbaum's "homologue-free" acetic anhydride was distilled several times through a six-section Young and Thomas evaporator-column stillhead. The apparatus was so arranged that the distillate could be collected in fractions and drawn off into bottles when required, and was carefully designed to prevent the entrance of moisture. Three fractions were finally obtained and the boiling points were immediately determined in an all-glass apparatus similar to that described by Edwards (*J. Soc. Chem. Ind.*, 1918, **37**, 38T) but having ground glass joints and a ground-in stopper, from which the thermometer was suspended by means of a platinum wire and a glass hook. The following results were obtained : Fraction 1, 100 c.c., b. p. 138·80°/760 mm.; fraction 2, 75 c.c., b. p. 139·36°/760 mm.; fraction 3, 50 c.c., b. p. 139·47°/760 mm.

A determination of the C.S.T.'s of fractions 2 and 3 with *cyclo*hexane gave results agreeing to within 0·03°. These two fractions were mixed and refractionated, the distillate having b. p. 139·41—139·47°/760 mm. and $d_{4^{\circ}}^{18^{\circ}}$ 1·0853 (compare Orton and Jones, *loc. cit.*, who gave b. p. 139·55°/760 mm., $d_{4^{\circ}}^{15^{\circ}}$ 1·0876, $d_{4^{\circ}}^{20^{\circ}}$ 1·0820). The material was kept in a well-stoppered bottle in a vacuum desiccator, and was used throughout the work.

cyclo*Hexane*. A sample of *cyclo*hexane (Poulenc Frères' "pur," m. p. 5·8°) was purified by repeated fractional freezing, and a final fraction obtained with m. p. 6·4°.

Carbon disulphide. A. R. material (B.D.H.) was subjected to a long shaking with mercury and distilled. It was then kept over phosphoric oxide for some time, and redistilled through the still-head described above. The final fraction obtained, b. p. 43·23°/760 mm., was immediately used for the experiments, and was almost free from the usual odour, having in fact a distinctly pleasant ethereal smell.

Petroleum. A high-boiling petroleum fraction was purified as described in a former paper (Jones, *loc. cit.*), a final fraction, b. p. 170—180°, being used. This was the material with which curve C, Fig. 2, was obtained. It was further purified by refluxing several times with the nitrating mixture, and distilled through an 8-bulb pear stillhead under reduced pressure. The fraction, b. p. 171—175°, so obtained gave results from which curve D, Fig. 2, was drawn. (*n*-Decane has b. p. 173°/760 mm.)

Acetic acid. The acetic acid used was Kahlbaum's "homologue-free" material. It was purified by fractional freezing, a final fraction, m. p. 16·60°, being used. A certain amount was treated in the manner described by Orton and Bradfield (J., 1924, **125**, 960); the fraction obtained after several distillations, m. p. 16·5°, was fractionally crystallised and finally had m. p. 16·60°.

All the above liquids were kept in well-stoppered glass bottles in desiccators over phosphoric oxide.

Determination of the Solubility Curves.—The synthetic method was used for the solubility determinations. Weighed quantities of the two liquids were sealed up in thin-walled glass bulbs, of about 2 c.c. capacity, and the miscibility temperature taken. Owing to the hygroscopic nature of acetic anhydride, great precautions were necessary in filling the tubes. This was done in a manner similar to that used by Ewins for formic acid (J., 1914, **105**, 350). The tube was first weighed empty, the *cyclo*hexane run in, the tube reweighed, the anhydride run in, and the tube sealed off in the blowpipe. The two portions were allowed to cool, and the whole was reweighed. By careful withdrawal of the delivery tubes, wetting of the walls could be avoided.

The temperature of mixing was determined as described in a former paper (Jones, *loc. cit.*). The best method for the determination of the clearing point was found to be the observation of the filament of an electric lamp placed behind the bath. Even then some difficulty was experienced, especially in the carbon disulphide system, but the temperature error involved was small. In the

critical region the mean of the temperature of the disappearance of the striations, which show up very clearly on shaking just below the miscibility temperatures, and the temperature of clouding was taken as the true miscibility temperature. If the tubes were vigorously shaken when near the mixing point there was found to be very little "lag," the greatest difference between the upper and lower readings being 0·1°. The thermometers used throughout this work were either standardised at the N.P.L. or compared with others so standardised, the correction for exposed stem being made.

The low-temperature miscibility points on the curve were determined in a bath of ether contained in an unsilvered Dewar flask of large capacity, and cooled below the necessary temperature by the addition of solid carbon dioxide.

The critical phenomena exhibited in the three cases differed markedly in degree. In the anhydride-petroleum system there was an almost complete absence of any critical phenomena; in the anhydride–*cyclo*hexane system the phenomena were more marked, but still comparatively slight; in the anhydride–carbon disulphide system the phenomena were most pronounced—in the neighbourhood of the C.S.T. very persistent emulsions formed on shaking, and there was a very intense and beautiful opalescence, which was strongest immediately above the C.S.T., and persisted for several degrees. This was presumably due to the similar

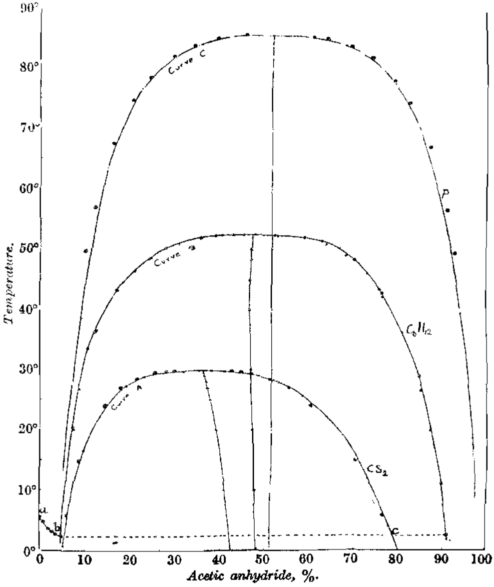
TABLE I.

Showing the miscibility temperature, T, corresponding to various proportions (% by weight) of acetic anhydride.

% $C_4H_6O_3$.	T.	% $C_4H_6O_3$.	T.	% $C_4H_6O_3$.	T.	% $C_4H_6O_3$.	T.
			Acetic anhydride–carbon disulphide.				
5·27	0·7°	*35·36*	*29·83°*	42·85	29·65°	58·57	25·7°
9·66	16·5	36·39	29·85	44·20	29·5	67·60	19·1
18·27	26·7	*36·93*	*29·80*	52·04	28·3	72·18	13·45
19·18	27·2	38·01	29·80	53·22	27·9	77·98	4·00
32·10	29·7	41·10	29·65				
			Acetic anhydride–*cyclo*hexane.				
7·20	20·4°	27·97	50·3°	52·25	52·37°	76·03	43·50°
10·40	33·5	39·03	52·25	58·83	52·00	84·71	29·00
12·00	36·2	43·01	52·40	62·77	51·40	89·83	11·00
16·90	43·1	*45·35*	*52·42*	70·16	48·30		
24·32	48·3	*47·84*	*52·45*				
			Acetic anhydride–petroleum.				
7·14	27·6°	30·83	82·0°	60·67	85·25°	79·85	77·35°
9·46	38·5	35·00	83·5	67·87	84·00	84·91	71·00
14·95	63·5	42·67	85·1	72·08	82·55	94·10	40·00
22·59	76·1	*50·33*	*85·47*	76·73	80·27	96·8	16·5
22·83	76·5	*53·50*	*85·52*	79·2	78·15	98·97	45·5
26·90	80·0						

densities and different refractive indices of the phases in this system. In all cases there were the usual flattening of the meniscus and appearance of flickering striations throughout the liquid just before

FIG. 1.



A. Mutual solubility of acetic anhydride and carbon disulphide.
B. ,, ,, ,, ,, ,, cyclohexane.
C. ,, ,, ,, ,, ,, petroleum.

The calculated solubility values are indicated by circles on curves A and C and by crosses on curve B; and the other points on each curve are experimentally determined.

the critical point was reached. Very similar results were obtained with acetic acid (Jones, *loc. cit.*).

Discussion of Solubility Curves.—The solubility results are shown in Table I and graphically in Fig. 1. Curves C, B, and A represent

the mutual solubility of the systems acetic anhydride–petroleum, acetic anhydride–*cyclo*hexane, and acetic anhydride–carbon disulphide, respectively. The mean-concentration curves for the three systems and, in the case of the system acetic anhydride–*cyclo*hexane, the freezing-point curve *abc* are also shown. The invariant point where solid *cyclo*hexane is in equilibrium with two liquid phases is at 2·269°. All the curves have the usual flattened-top form, and in two of the systems (*cyclo*hexane and petroleum) the mean-concentration curves are almost parallel to the temperature axis, the effect of temperature on the solubility of acetic anhydride in both phases being almost the same. In those two systems in which the freezing-point curve is very low (petroleum and carbon disulphide), an attempt was made to see whether either of these systems showed any inclination to become closed curves, with a complete miscibility area, at lower temperatures, but at the lowest temperature used (solid carbon dioxide and ether) there was no indication of such a trend.

Table II contains the critical solution data, *i.e.*, the critical solution temperatures and the critical solution concentrations expressed in several ways.

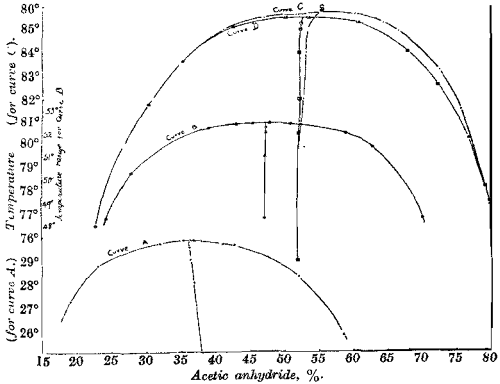
TABLE II.

		Critical concentration of acetic anhydride, %.		
	C.S.T.	By wt.	By vol.	By mols.
Acetic anhydride–carbon disulphide	29·83°	36·17	39·86	29·69
Acetic anhydride–*cyclo*hexane	52·45	47·33	39·31	40·63
Acetic anhydride–petroleum	85·50	52·11	42·76	62·47

The Mean-concentration Curve.—It is well known that if the mean value of the concentrations (as g. per 100 g. of solution) of the two coexisting phases is plotted against the corresponding temperature, in a large number of cases a curve is obtained which differs very slightly, if at all, from a straight line. Certain important qualifications must be made to this statement. Frequently, quite marked irregular deviations from the mean-concentration curve have been observed in the neighbourhood of the C.S.T. It is precisely in this region that the accuracy of the experimental observations of the miscibility temperature is greatest : in all the systems investigated here it was possible to read the miscibility temperature to about 0·02° in this region. On the other hand, at this point the curve is very flat, and considerable changes in the concentration produce very slight miscibility-temperature changes. In other cases, the mean-concentration line is definitely curved only in the immediate neighbourhood of the C.S.T. It will be shown here that this can frequently be ascribed to the presence of

an impurity, a third component, in the system. Most marked deviation is observed throughout the mean-concentration curve when the system exhibits a lower C.S.T. It is quite possible that this may be due (at least partly) to impurities produced in the system, *e.g.*, the formation of a hydrate in a system of which water is one component. The curvature of the mean-concentration line in the direction of the more volatile component with increasing temperature may, in some instances, be due to neglect of the correction to the concentration necessitated by the unequal volatility of

FIG. 2.



Curves A, B, and C are enlargements of A, B, and C (Fig. 1). Curve D is based on results obtained after further purification of the petroleum which originally gave curve C.

the components. In many cases quoted in the literature, the temperatures have not been estimated in the critical region to less than 0·1°. It is of interest, therefore, that, if the curves are accurately determined, no irregular deviations can be detected in the immediate neighbourhood of the C.S.T. (see large-scale curves, Fig. 2).

Furthermore, by the use of calibrated cylindrical tubes of 2—3 c.c. volume it was found possible to determine the critical concentrations to within about 1% by direct observation of the relative volumes of the phases at about 0·05° below the miscibility tem-

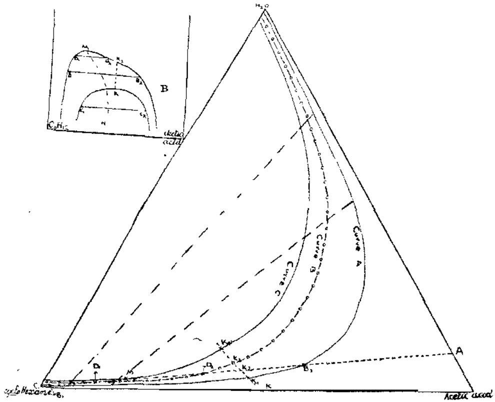
peratures : at the critical solution concentration the volumes of the coexisting phases should be equal. (It is evident, from work now proceeding, that the critical solution concentrations could be determined by this method, using larger liquid volumes, with very considerable accuracy.) We were thus able to compare the values of the critical concentration, as given by the point of intersection of the solubility curve and the mean-concentration curve, with the values obtained by direct volumetric observation. In Table I, the two concentrations in each system which are italicised are those in which a determination of phase volume had shown that the critical solution point was intermediate in concentration between them; *e.g.*, in the carbon disulphide–acetic acid system the 36·93% mixture gave a lower layer greater than the upper; in the 35·36% mixture the reverse was the case.

It is clear from these results that in the carbon disulphide–acetic anhydride system, although the curvature of the mean-concentration line was considerable, it intersected the solubility curve in the critical solution concentration point. This affords evidence that the curvature is not due to impurities in the system, as might have been suspected on the grounds that water in the acetic anhydride would undoubtedly have had the effect of curving the mean-concentration line in this same direction. A curvature of this line may then be due to impurities in the system, or it may be inherent in the system. A determination of the critical concentration by alternative methods distinguishes these two cases. If the critical phenomena are distinct and impurity is present in fairly large quantity, the diminution of this alone may serve to indicate whether the maximum point on the curve which is always one terminus of the mean-concentration curve is the C.S.T.

These results may be compared with the methyl alcohol–hexane curve determined by Rothmund (*Z. physikal. Chem.*, 1898, 26, 433). Neglecting the points in the immediate neighbourhood of the C.S.T., and drawing a straight line through the mean concentrations at lower temperatures, he obtained values for the critical solution concentrations and the C.S.T. From his results it is clear that if the values in the neighbourhood of the C.S.T. are used and the mean concentrations plotted, the line shows quite definite curvature leading to a maximum temperature on the solubility curve at quite a different concentration from that of the critical solution point. This is undoubtedly due to a trace of water in the methyl alcohol used. His results may be compared with those obtained by one of us in the system acetic acid–*cyclo*hexane (Jones, *loc. cit.*, p. 1387, Fig. 2) : with only 0·28% of water in the acetic acid, the maximum temperature on the curve is no

longer that of the C.S.T., the concentration corresponding to the maximum temperature is approximately 75% *cyclo*hexane, and the critical solution concentration is approximately 50% (curve B, *loc. cit.*). The effect is much more marked when the proportion of water in the acetic acid is 1·2% (curve C, *loc. cit.*). That this is the result to be expected can be seen most clearly from a ternary diagram of the system. On Fig. 3A the curves A, B, and C represent typical isothermal curves that would be obtained in the system acetic acid–water–*cyclo*hexane at three increasing temperatures.

FIG. 3B. FIG. 3A.



Owing to the fact that the acetic acid distributes itself mainly in the aqueous phase, the tie-lines would run somewhat as marked in broken lines for the curve A, and the ternary critical temperature line would be represented by KK_4. AC represents the composition of all mixtures of *cyclo*hexane and an aqueous acetic acid, and the points where this line cuts the projection of the binodal curves will be miscibility points of the system. B_1 and B_2 at one temperature, and D_1 and D_2 for a higher temperature, represent four of these points, which in Fig. 3B are plotted in a two co-ordinate system. At the temperature of the isothermal curve C, AC becomes tangential at the point M, and this point would be the maximum point as plotted on Fig. 3B. K_2 is represented in the same figure

as the C.S.T. for the aqueous acetic acid represented by A on Fig. 3A, and this corresponds to the point where the line AC cuts the critical line.

In Fig. 3B, the line MN represents the mean-concentration curve for Curve B, Fig. 3B (*cyclo*hexane–aqueous acetic acid). Only one case can occur in which, in the presence of a third component, the maximum point of the curve plotted in a two co-ordinate system would coincide with the critical point, and that is when the ternary critical solution concentrations are such that the line AC, Fig. 3A, is tangential to the binodal curve at the ternary critical solution point. The difference in concentration of the maximum point M and the critical solution point K_2 is dependent largely on the distribution ratio of the third component between the two phases. The volumes of the phases would be equal at a temperature just below K_2 for a system of this composition, and quite different at a temperature just below M for a system whose composition is represented by this point. This is clearly seen from Fig. 3A.

In the *cyclo*hexane–acetic anhydride system, the mean concentration curve (in this case, almost a straight line) cuts the solubility curve in a point which is in agreement with the critical solution point obtained by direct volumetric observation.

In the petroleum–acetic anhydride system the curve (mean concentration curve, corresponding to Curve C, Fig. 2) again showed marked deviation from linearity, but in the opposite direction to that in the case of carbon disulphide–acetic anhydride. When the phase volumes at the concentration represented by the point of intersection of the solubility curve (point S, Fig. 2) were compared, a large excess of anhydride was found, *i.e.*, the volume of the lower layer was much greater than that of the upper layer, at a temperature very close to the miscibility temperature. Observations of volume indicated that the critical concentration was on the linear extension of the lower points of the mean-concentration line. From the direction of deviation of the line it seemed probable that the impurity present would be a higher fraction. The petroleum was treated again with the nitrating mixture and carefully re-fractionated, as described above, and the solubility determinations were repeated. The solubility curve obtained is represented as Curve D, Fig. 2. As is seen, the curvature in the mean-concentration line was reduced considerably, thus affording evidence that an impurity of this type was present in the original fraction.

In view of these results, it can be concluded that, in the systems examined here, in two cases the mean-concentration line is straight within the limits of experimental error, right up to within 0·02° of the C.S.T., and in the other case the line has a definite curvature

which is not due to impurities. It would seem that the arguments used in this section would apply if the impurities were produced in the system by, for instance, chemical combination between the components, or by polymerisation of one or other of the components; and in this way it could be determined whether the marked curvature of the mean-concentration line in the case of, *e.g.*, nicotine and water near its lower C.S.T. was due to the presence of the hydrate as impurity.

Table III contains the figures from which the mean-concentration curves were plotted.

TABLE III.

Temp.	C_1.	C_2.	Mean.
Carbon disulphide–acetic anhydride.			
0°	5·00	80·00	42·50
10	7·20	74·67	40·94
20	11·87	66·43	39·15
25	16·20	59·60	37·90
27	18·70	55·70	37·20
28	20·87	53·00	36·94
29	24·33	48·37	36·35
29·5	28·40	44·20	36·30
29·84	36·17	36·17	36·17†
*cyclo*Hexane–acetic anhydride.			
0°	5·00	91·0	48·00*
10	6·00	90·0	48·00
20	7·23	87·67	47·45
30	9·37	84·27	46·82
40	14·40	78·87	46·69
45	18·67	74·57	46·67
48·3	24·32	70·16	47·24
50	27·17	67·08	47·13
51	30·58	64·17	47·37
52	35·90	58·83	47·36
52·25	39·03	55·66	47·34
52·45	47·33	47·33	47·33†

Temp.	C_1.	C_2.	Mean.
Petroleum–acetic anhydride. (Curve D, Fig. 2.)			
0°	5·00	97·26	51·13
10	5·60	96·9	51·25
20	6·43	96·60	51·51
30	7·69	95·37	51·53
40	9·17	94·10	51·63
50	11·00	92·32	51·66
60	13·50	89·90	51·70
70	18·00	85·60	51·80
75	22·00	82·00	52·00
80	26·90	77·17	52·03
82	30·85	73·34	52·09
84	36·70	67·83	52·26
85	41·75	63·08	52·41
85·25	44·30	60·70	52·50
85·50	52·11	52·11	52·11†
Petroleum–acetic anhydride. (Curve C, Fig. 2.)			
80°	26·90	77·33	52·12
82	30·66	74·66	52·66
84	36·50	70·01	53·25
85	41·20	65·80	53·50
85·5	46·66	61·66	54·16
85·75	56·00	56·00	56·00‡

* Extrapolated.

† Extrapolated values read from intersection of solubility curve and mean-concentration curve.

‡ Maximum temperature: concentrations are not critical.

The Law of Corresponding States.

In view of the facts that we are dealing with the solubility curves of acetic anhydride in a series of closely related non-polar solvents, and that acetic anhydride is, as far as can be seen, a non-associated substance (see next section), it seemed desirable to investigate whether at corresponding C.S.T.'s the saturation concentrations were also corresponding. Rothmund (*loc. cit.*) investigated this question for a series of 12 different liquid mixtures, all of which

contained an associated compound, and concluded that the law of corresponding states was not valid.

In Table IV are the results of the calculation of the reduced concentrations at various reduced temperatures extending over the whole solubility curve up to within 0·1° of the C.S.T.

TABLE IV.

1. Reduced temp.	2. System.	3. Temp.	4. C_1.	5. C_1/C_k.	6. C_1 (calc.).	7. C'_1/C'_k.	8. C_1 (calc.).	9. C_2.	10. C_2/C_k.	11. C_2 (calc.).	12. C'_2/C'_k.	13. C_2 (calc.).
	I	20·68°	31·58	0·8732	31·19	0·8149	29·93	42·00	1·161	41·88	1·278	43·96
0·9995	II	52·28	39·75	0·8399	40·80	0·7341	41·80	55·17	1·166	54·80	1·369	53·89
	III	85·32	45·50	0·8732	44·92	0·7672	45·79	59·84	1·148	60·34	1·368	58·47
	I	29·63	28·67	0·7929	29·14	0·7098	28·03	44·00	1·217	43·71	1·387	46·68
0·999	II	52·13	37·83	0·7993	38·13	0·6772	38·74	57·75	1·220	57·20	1·522	55·84
	III	85·14	43·00	0·8252	41·99	0·6933	43·01	62·08	1·191	62·98	1·505	60·69
	I	29·22	26·00	0·7190	26·91	0·6201	25·72	46·75	1·293	45·79	1·550	49·09
0·998	II	51·80	35·00	0·7390	35·22	0·5994	35·82	60·30	1·275	59·93	1·600	58·04
	III	84·78	40·30	0·7734	38·77	0·6203	39·85	64·09	1·230	65·98	1·641	63·58
	I	28·32	21·72	0·0006	23·07	0·4898	21·74	51·83	1·433	49·69	1·900	54·40
0·995	II	50·82	29·75	0·6287	30·18	0·4714	30·94	64·75	1·368	65·03	2·045	63·13
	III	83·7	35·67	0·6844	33·24	0·5096	34·32	68·87	1·322	71·60	2·033	67·53
	I	26·80	18·40	0·5087	19·75	0·3979	18·30	56·20	1·553	57·12	2·264	60·25
0·99	II	49·19	25·67	0·5424	25·82	0·3843	26·43	68·70	1·452	69·71	2·443	68·14
	III	81·91	30·58	0·5868	28·43	0·4048	29·90	73·00	1·413	76·75	2·563	69·62
	I	23·77	14·90	0·4120	15·94	0·3090	14·46	61·5	1·700	56·94	2·820	68·28
0·98	II	45·94	20·57	0·4347	20·85	0·2882	21·40	73·67	1·557	75·30	3·114	74·05
	III	78·33	24·77	0·4753	22·96	0·3025	24·55	70·00	1·517	82·91	3·457	71·52
	I	20·75	12·33	0·3409	13·24	0·2482	11·82	65·40	1·808	60·97	3·336	73·47
0·97	II	42·69	16·57	0·3501	17·32	0·2184	18·06	76·73	1·621	79·00	3·670	78·34
	III	74·75	21·20	0·4068	19·07	0·2473	20·41	82·15	1·577	80·98	4·236	72·70
	I	14·69	8·90	0·2461	9·88	0·1725	8·74	71·40	1·974	64·60	4·405	82·81
0·95	II	36·18	12·00	0·2536	12·93	0·1518	13·39	81·27	1·718	84·33	4·831	85·98
	III	67·58	16·67	0·3199	14·24	0·1838	15·36	86·90	1·667	92·87	6·095	72·85
	I	5·60	6·17	0·1706	7·09	0·1161	6·29	77·17	2·134	68·59	5·967	94·02
0·92	II	26·41	8·33	0·1760	9·28	0·1011	9·60	85·67	1·810	89·74	6·655	93·56
	III	56·82	12·60	0·2418	10·22	0·1325	11·09	90·93	1·745	98·80	9·181	71·96
	I	−0·45	5·04	0·1393	6·03	0·0937	5·24	80·17	2·217	70·52	7·134	99·21
0·90	II	19·90	7·17	0·1515	7·89	0·0800	8·12	87·73	1·854	92·24	7·957	97·30
	III	49·65	10·92	0·2095	8·69	0·1127	9·45	92·53	1·775	101·60	11·39	71·75

System I: Acetic anhydride–carbon disulphide.
" II: " " –*cyclo*hexane.
" III: " " –petroleum.

From the experimental results, by the synthetic method, the values of the *saturation concentrations*, C_1 and C_2, *are obtained* in g. per 100 g. of solution. C_k represents the critical solution concentration expressed in the same way. Cols. 5 and 10 give the values of the reduced concentrations C_1/C_k and C_2/C_k thus expressed. Cols. 6 and 11 contain the values of C_1 and C_2 calculated by multiplying the average reduced concentration for each reduced temperature by C_k. For the C_1 values there is an average deviation of 1·12%. *For the C_2 values, the deviation*, although small at the higher reduced temperatures, becomes very large at the lower temperatures.

It is possible that concentrations would be more correctly expressed as g. per 100 c.c. of solution. It can be shown (Rothmund *loc. cit.*) that if they were so expressed, and if the law of corresponding states held, then the expression $C_1(100 - C_k)/C_k(100 - C_1$

should be constant. It is obvious from the form of this expression that this is really the reduced concentration if the actual concentration is expressed as g. of one component per 100 g. of the second component, usually considered as solvent. The reduced concentrations calculated in this way are given in cols. 7 and 12 under the headings C'_1/C'_k and C'_2/C'_k (acetic anhydride being considered as solute). Cols. 8 and 13 give the values of C_1 and C_2 calculated from the average reduced concentrations expressed in this way. The deviations for C_1 are smaller than before, and those for C_2 again show very large variations at lower reduced temperatures.

The fair constancy of the C'_1/C'_k values, and the possibility of the calculation of the C_1 value, seemed worthy of fuller consideration. For reduced temperatures of 0·998 to 0·9995, in the neighbourhood of the C.S.T.'s, the deviations are within the experimental error of the method used. For 0·98—0·998, the deviations are less, but it is in this region of the curves that the accuracy should be greatest, and the deviation cannot be ascribed to experimental error. For 0·90—0·98, the deviation tends to increase; this covers a region of the curves in which there is difficulty in observing the exact miscibility temperature, but the deviations are much greater than could be accounted for on these grounds.

The calculated values of C_1 are shown in Fig. 1, and are in general agreement with experimental values. The results indicate that the law of corresponding states holds with a fair degree of accuracy up to certain concentrations of acetic anhydride, *viz.*, 46·75%, 60·30%, and 64·09% in carbon disulphide, *cyclo*hexane, and petroleum, respectively. This agreement is rendered more striking when it is considered that the C.S.T.'s concerned varied from 29·83° to 85·50°, and the critical solution concentrations from 36·17% to 52·11% of acetic anhydride.

In spite of the deviations between found and calculated values of C_2, it is clear that, in general, the mean-concentration curve can be regarded as approximately linear, for even in the case of carbon disulphide–acetic anhydride the maximum error involved is only about 1%. If, therefore, in addition to the critical solution data, the solubility at one other temperature is determined, so as to give one other point on the mean-concentration line, the rest of the solubility curve can be calculated. This has been done, and the calculated values of C_2 are in Table V (col. 4), and represented in Fig. 1. The deviations (col. 5) are of the same order of magnitude as those found in the calculation of C_1, the average for the three systems being 0·89%.

In this way the whole solubility curves can be calculated with

TABLE V.

Temp.	$C_1 + C_2$ (calc.).	C_1 (calc.).	C_2 (calc.).	Deviation.
		Carbon disulphide–acetic anhydride.		
−0·45°	85·21%	5·24%	79·97%	+0·20%
5·60	82·64	6·29	76·35	−0·82
14·69	78·77	8·74	70·03	−1·37
20·75	76·20	11·82	64·38	−1·02
23·77	74·92	14·46	60·46	−1·04
26·80	73·63	18·30	55·33	−0·87
28·32	72·98	21·74	51·24	−0·59
29·22	72·60	25·72	46·88	+0·13
29·53	72·46	28·03	44·43	+0·43
29·68	72·41	29·93	42·48	+0·48
		*cyclo*Hexane–acetic anhydride.		
19·90	94·90	8·12	86·78	−0·95
26·41	94·85	9·60	85·25	−0·42
36·18	94·78	13·39	81·39	+0·12
42·69	94·73	18·06	76·67	−0·06
45·94	94·70	21·40	73·30	−0·37
49·19	94·68	26·43	68·25	−0·45
50·82	94·67	30·94	63·73	−1·02
51·80	94·66	35·82	58·84	−1·46
52·13	94·66	38·74	55·92	−1·83
52·28	94·66	41·80	52·86	−2·31
		Petroleum–acetic anhydride.		
49·65	103·46	9·45	94·01	+1·48
56·82	103·63	11·09	92·53	+1·60
67·58	103·84	15·36	88·48	+1·58
74·75	104·00	20·41	83·59	+1·42
78·33	104·06	24·55	79·51	+0·51
81·91	104·14	29·90	74·24	+0·64
83·70	104·18	34·32	69·86	+0·99
84·78	104·20	39·85	64·35	+0·24
85·14	104·22	43·01	61·21	−0·87
85·32	104·22	45·79	58·43	−1·41

Col. 3 contains the values of C_1 calculated from the reduced concentrations C'_1/C'_k (Col. 8, Table IV). Col. 2 contains the calculated values of $C_1 + C_2$ assuming a linear mean-concentration line. Col. 4 contains the C_2 values calculated as the difference between the foregoing.

very fair precision, as seen from the coincidence of the calculated and observed solubility curves in Fig. 1.

This research is being extended to the determination of the mutual solubility of acetic anhydride with a larger range of non-polar liquids (*e.g.*, a series of the saturated hydrocarbons), and to that of other non-associated polar liquids, such as aniline and nitrobenzene, in these non-polar solvents.

The Influence of Acetic Acid on the C.S.T.

This part of the work was undertaken in the hope that the C.S.T might be utilised as a means of estimating acetic acid present as an impurity in the anhydride. The procedure was to introduce into the pure anhydride a known amount of acetic acid, and to

determine the effect on the C.S.T. After the introduction of the liquids by means of pipettes, graduated to deliver critical proportions, the experimental tubes were sealed off as before and the miscibility temperatures taken.

From the curves obtained it was found that proportions of acetic acid (up to 0·5%), such as might occur in the anhydride as impurity, have very little effect on the C.S.T., and in no case was the lowering greater than 1° for 5% of acid. There was distinct flattening of the upper end of all three curves, making the lowering due to the first 1—2% of acid scarcely detectable, and rendering the method of little value. On the other hand, 1% of anhydride in acetic acid raises its C.S.T. with petroleum by 2°, *i.e.*, 0·1% of anhydride in acetic acid could be detected.

TABLE VI.

The effect of acetic acid on the systems acetic anhydride and (1) *cyclo*hexane, (2) carbon disulphide, (3) petroleum.

(1) Acid, %.	(1) C.S.T.	(2) Acid, %.	(2) C.S.T.	(3) Acid, %.	(3) C.S.T.
—	*52·45°	—	29·83°	—	85·50°
2·94	51·80	5·28	28·93	24·90	81·70
4·05	51·70	23·14	25·03	48·65	72·80
22·37	45·70	40·66	20·53	72·87	60·45
50·6	†33·75	59·97	14·68	100	39·2
50·98	34·15	73·91	10·98		
74·6	19·95	100	4·20		
87·1	12·30				
100	4·30				

* This C.S.T. was redetermined after a period of 4½ months, and the variation was found to be less than 0·02°. This proves the absence of any moisture in the original anhydride and its exclusion during filling.

† The acid in this case was that specially purified by Orton's method (see above). The corresponding curve is very slightly lower than that given by the other acid, the temperature difference at this concentration being, however, less than 0·1°.

Internal Pressure and Solubility.

It has been shown, *e.g.*, by Hildebrand ("Solubility," p. 110), that the internal pressure, K, may as a first approximation be put proportional to $\gamma/V^{\frac{1}{3}}$. The calculated value of this function for acetic anhydride at 20° is 7·175, which places it a little higher than benzene (6·48) in the internal-pressure series calculated in this manner. Carbon disulphide has the much higher value 8·7 and hexane and *cyclo*hexane the values 3·80 and 5·56, respectively. Acetic acid gives 5·75 for the dimeric and 7·24 for the monomeric molecule. From Vespignani's value (*Gazzetta*, 1903, **33**, i, 77) for the critical constants of acetic anhydride, *viz.*, $t_c = 296°$, $p_c = 46·2$

atms., the value of a in van der Waals's equation is calculated to be 3967×10^{-5}, and a/V^2 becomes $441{\cdot}8 \times 10^{-8}$, where V is the molecular volume at 20°. This places the substance just below benzene (472×10^{-8}) in the internal-pressure series thus calculated; the values of $a/V^2 \times 10^8$ for hexane and carbon disulphide are 290 and 610, respectively. Both methods of calculation lead *to a similar relative position for acetic anhydride in the series.*

Although there is a considerable difference in internal pressure between the anhydride and hexane, yet its proximity to benzene does not agree with the solubility of the anhydride in the solvents used in this research; it is very close to *cyclo*hexane in the series, and moreover, carbon disulphide has a considerably greater internal pressure. It should be noted, however, that the internal pressure of acetic anhydride so calculated is not at *all* what one would expect from the value of its dielectric constant.

Summary.

(1) The mutual liquid-solubility curves for the binary systems composed of acetic anhydride with carbon disulphide, *cyclo*hexane, or a saturated petroleum fraction (decane) have been determined.

(2) The degree of concordance of the solubility values with the theory of corresponding states has been discussed. The systems investigated show good agreement with the theory in the phase rich in the less polar constituent.

(3) The mean-concentration curves for these systems are linear in two cases and slightly curved in one case (carbon disulphide). The possible causes for deviation from linearity are discussed, and the conclusions tested by a direct determination of the critical solution concentration in these systems.

(4) The position of acetic anhydride in the internal-pressure series is considered in relation to the solubility results.

(5) The effect of acetic acid on the critical solution temperatures is evaluated.

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CLI.—*Some Physical Properties of Acetic Anhydride and Related Substances and their Constitutional Significance.*

By DAVID CHARLES JONES.

Determination of the Molecular Weight of Acetic Anhydride in Benzene and in cyclo*Hexane.*—Apart from Pickering's cryoscopic determination (J., 1893, **63**, 1000) of the molecular weight of acetic anhydride in acetic acid, no results on the molecular weight of acetic anhydride are recorded in the literature. In this research the lowering of the freezing points of *cyclo*hexane and benzene by acetic anhydride was determined, and the results are shown in Tables I and III, respectively. In all cases, in dilute solution the anhydride gives values corresponding to the normal molecular weight (102).

TABLE I.

Solvent: *cyclo*hexane, m. p. 6·4°.

Conc.	F. p.	Lowering of f. p.	*M* (found).	*M* (found) / *M* (calc.)
0·335	5·8°	0·603°	111·2	1·09
0·684	5·25	1·147	119·3	1·17
1·087	4·6	1·784	121·8	1·20
2·203	3·25	3·153	139·7	1·37
2·947	2·66	3·742	157·4	1·54
(5·33)	(2·269)	(4·131)	(272·5)	(2·67)

The concentration in Table I is expressed in g. per 100 g. of solvent. The molecular lowering of the freezing point of *cyclo*hexane is assumed to be 200 (Mascarelli and Benati, *Gazzetta*, 1909, **39**, ii, 642). The last values in Table I correspond to the invariant point, where solid *cyclo*hexane is in equilibrium with the two liquid phases; this was determined in the ordinary freezing-point apparatus by adding a sufficient quantity of acetic anhydride to give a two-liquid layer system, and precautions were taken, by a very slow temperature adjustment, to ensure the two liquid layers being in equilibrium. The corresponding concentration of the *cyclo*hexane-rich phase was read from the solubility curve (preceding paper). The supercooling in any determination did not exceed 0·05°, spontaneous freezing occurring in nearly all cases at this point. A slow stream of dried air was passed through the annular space round the stirrer to prevent absorption of moisture during the determination. Only the results for the very low concentrations are regarded as giving values for the molecular weight of acetic anhydride in this solvent; the rapid increase in the values with increasing concentration probably illustrates merely the positive deviation of the system from Raoult's

law, since the two liquids form a two-liquid layer system. (The same value for the freezing point would be obtained whatever the concentrations of the solutions between 5·33% and 90·87% of acetic anhydride.)

It is interesting to compare these results with those obtained for aniline and acetic acid in *cyclo*hexane (see Table II). The theoretical

TABLE II.

	Conc.	*M* (calc.).	*M* (found).	*M* (found)/*M* (calc.).
Acetic acid *	0·86	120	127·7	1·064
	3·49	120	140·0	1·166
Aniline *	0·40	93·1	106	1·139
	3·05	93·1	136	1·461
Acetic anhydride	0·335	102	111·2	1·09
	2·947	102	157·4	1·54

* Turner, "Molecular Association," pp. 128, 143.

value for the molecular weight of acetic acid is taken as that of the double molecule. The values for the so-called "association factor" in the case of aniline and acetic anhydride are very similar in solutions of about the same concentrations, probably because they both exhibit a positive deviation from Raoult's law to the extent of forming a two-layer system with similar C.S.T.'s, *e.g.*, aniline–*cyclo*hexane, 41°, 49·72% aniline (Chavanne and Simon, *Compt. rend.*, 1919, **168**, 1111); acetic anhydride–*cyclo*hexane, 52·45°, 47·33% anhydride (Jones and Betts, preceding paper). For acetic acid the association is much smaller in solutions of corresponding concentrations. In this case the liquids are completely miscible at the temperature reached by the freezing-point curve, but the metastable liquid–liquid solubility curve lies just below the freezing-point curve (Jones, J., 1923, **123**, 1374).

When acetic anhydride is dissolved in benzene the molecular weight is normal up to a concentration of 3·8%, with a slight tendency to increase at higher concentrations. In this case, although the solvent is similar in type to *cyclo*hexane, the two differ in that benzene is completely miscible with the anhydride.

TABLE III.

Solvent: benzene.

Conc.	Lowering of f. p.	*M* (found).	*M* (found)/*M* (calc.).
1·539	0·783°	98·30	0·97
2·205	1·090	101·20	0·99
3·761	1·770	106·1	1·04

The temperature coefficients of "molecular cohesion" and of "molecular surface energy," as determined by Walden and Swinne (*Z. physikal. Chem.*, 1913, **82**, 296) for the group of liquids concerned

TABLE IV.

	Temp. coeff. of molecular cohesion, obs.	calc.	Temp. coeff. of molecular surface energy, obs.	calc.
Acetic anhydride	0·0177	0·0177	2·13	2·25
Acetic acid	0·0077	0·0155	0·95	2·11
Carbon disulphide ...	0·0155	0·0151	2·08	2·09
Aniline	0·0177	0·0188	2·05	2·20
Hexane	0·0201	0·0201	2·21	2·30

in this paper, are given in Table IV. They support the conclusion reached from the freezing-point determination—acetic anhydride and aniline behave as "normal" liquids, whereas acetic acid gives about half the calculated values. Hexane and carbon disulphide are typical "normal" liquids. It has been suggested by Sidgwick ("Electronic Theory of Valency," p. 137) that it is the absence of co-ordinating hydrogen which accounts for the fact that ethyl ether, as judged by its properties in the pure state, is unassociated, as contrasted with, for instance, ethyl alcohol. Acetic anhydride probably affords another instance of this: there is no acceptor atom present.

The Parachor and the Constitutions of Acetic Acid, Acetic Anhydride, and Ethyl Alcohol.—Sugden (J., 1924, **125**, 1177) has compared molecular volumes at the same value of surface tension, and shown that these volumes can be calculated from values given to the various atoms present in the molecule if account is also taken of certain constitutive effects. From Orton and Jones's value for the density ($d_{4^\circ}^{20^\circ}$ 1·0840) and Ramsay and Shields's corrected value for the surface tension ($\gamma_{20^\circ} = 32{\cdot}69$) the parachor for acetic anhydride is found to be 225·5. The calculated value is obtained thus: 4C = 19·2; 6H = 102·6; 1 double bond + 1O = 43·2; 2O + 1 double bond (as in the esters) = 60·0; total = 225·0. Acetic anhydride therefore gives a molecular volume value as if it were a ketonic ester. The parachor for acetic acid is fairly constant if it is calculated from Bennett's values for the surface tension at 20° and 130° (J., 1915, **107**, 315), and from Ramsay and Shields's values, as corrected by Sugden (J., 1924, **125**, 38), for other temperatures.* The following table is based on the foregoing data, together with a molecular weight of 60, and with Young's values for the orthobaric densities:

Temp.	γ.	P (obs.).	Temp.	γ.	P (obs.).
20°	27·90	131·5	190°	11·45	133·9
130	17·01	132·6	220	8·71	134·9
160	14·21	133·5	280	2·83	136·9

* Ramsay and Shields's value for γ at 20° seems to be much too low; their corrected value at 130° is 17·05 (compare Bennett's 17·01).

Clearly the dissociation of the dimeric molecule occurs to a ver slight extent up to temperatures well above the boiling point.

The constancy in the values of K (total molecular surface energy obtained from Ramsay and Shields's values for the four highe aliphatic acids seems to indicate that in these acids also we hav stable dimeric molecules at the ordinary temperature, *e.g.*, butyri acid gives $K = 1100$, 1072, and 1088 for temperature ranges o 16—46°, 46—78°, and 78—132°, respectively (Bennett and Mitchell *Z. physikal. Chem.*, 1913, **84**, 475).

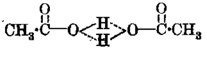
Using Ramsay and Shields's values for the aliphatic acids, an correcting them by the addition of 1 dyne, we obtain the followin results for the observed parachors at 20° :

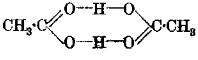
	P (obs.).	P_1 (calc.).	P_2 (calc.).	Δ_1.	Δ_2.
Acetic acid	131·5	141·2	138	−6·5	−13·0
Propionic acid	170·5	180·2	177	−6·5	−13·0
n-Butyric acid	208·6	219·2	216	−7·4	−14·8
n-Valeric acid	248·7	258·2	255	−6·3	−12·6

P_1 is calculated by summing the atomic constants + one doubl bond, as for the ordinary formula $CH_3{\cdot}CO{\cdot}OH$; P_2 is the paracho calculated on the assumption that the two oxygen atoms have th same value as in the esters. Δ_1 is the difference (a contraction between P (obs.) and P_2 (calc.), and Δ_2 is the corresponding differ ence for the dimeric molecule.

Although the data for the higher members may not be ver accurate, yet there is distinct evidence that the structure of th associated dimeric molecule—an association which undoubtedl concerns the two carboxyl groups—involves a constant large con traction in the observed molecular volume. On the basis of thi evidence alone, it cannot be decided whether this contraction i partly or wholly due to the association, for the parachor is determine on the associated acid, and gives no information regarding th volume of the single carboxyl group.

It is possible to account for these very large contractions on th assumption that the association involves single-electron linking (Sugden, J., 1927, 1173). In this connexion two formulæ tha have been proposed for the associated acetic acid are of interest (I) (Hantzsch, *Ber.*, 1927, **60**, 1933), and (II) (Pfeiffer, " Organisch Molekülverbindungen," 2nd Edition, p. 128). The calculate parachor for formula (I), if the dotted lines represent single-electro

(I.) 

 (II.)

co-ordination bonds, is 276 (see P_2, above), plus 11·6 for a 4-mem bered ring, minus 24·8 for the two co-ordination bonds, *i.e.*, 262·8

units, whereas the observed parachor is 263·0 (M = 120). This assumes that the two pairs of oxygen atoms have the same value as in the esters. Similarly for (II) we have for the calculated value 282·4 (see P_1, p. 1196), plus 5·8 for an 8-membered ring, minus 24·8 for the two co-ordination bonds, *i.e.*, 263·4 units. This does not assume the contraction for the two pairs of oxygen atoms as in the esters.

In spite of the good numerical agreement, it seems doubtful whether formulæ (I) and (II), involving 4-ring and 8-ring structures with two singlet-electron bonds, would account for the great stability of the dimeric molecules of the fatty acids, although both formulæ appear to be in agreement with other properties of acetic acid. Formula (I) has the character of an ester, and as such would account for the low dielectric constant, the non-reactivity of the carbonyl groups, and the large solubility values in petroleum. In both formulæ there would be no tendency to associate further than the dimeric molecule.

It is of interest to compare the corresponding values for ethyl alcohol. Taking Richards and Carver's results (*J. Amer. Chem. Soc.*, 1921, **43**, 827) for the surface tension at 20°, and Ramsay and Shields's corrected results for the higher temperatures, we have the following values :

Temp.	20°	80°	110°	140°	170°	200°	230°
P (obs.)	126·7	128·7	128·1	129·4	130·1	130·9	132·9

The theoretical value for ethyl alcohol is 132·2. It is evident that the values increase more rapidly with rise in temperature than do the corresponding values for acetic acid, but apparently dissociation in the liquid is not complete even at 200°. A contraction also occurs here, and at 20° it is equal to − 5·5 units for the single molecule, or − 11 units for the double. This result is not inconsistent with the view that association of an alcohol takes place by co-ordination through hydrogen, if this is accomplished hy a singlet co-ordination bond, *i.e.*, C_2H_5–O–H—OH·C_2H_5. One such bond requires a contraction of 12·4 units; this would mean, apparently, that the ethyl alcohol at 20° was, on the average, in the dimeric form.

The Solubility of some C_4 *Compounds in Saturated Hydrocarbons.*— The greater solubility of ethyl ether than ethyl alcohol, and of acetic acid than its anhydride, in saturated hydrocarbons is what would be expected from the dielectric constants : Ethyl alcohol (associated) $\epsilon_{20°}$ = 25·8, ether $\epsilon_{20°}$ = 4·4, acetic acid (associated) $\epsilon_{18°}$ = 6·29, acetic anhydride $\epsilon_{20°}$ = 20·5. The associated hydroxyl groups in alcohols are more polar than the ethereal oxygen group. The association of the acid takes place differently, the residual

affinity of the active groups being conjugated in such a way that the resulting compound is less polar than its anhydride.

The Effect of Oxygen-containing Groups on the Solubility in Water of C_4 *Aliphatic Compounds.*—It should be possible to obtain important information concerning the structure of groups containing oxygen from a study of the solubility in water of the compounds containing them. Table V gives a list of some C_4 and C_5 compounds and their solubility in water at 20° (Landolt–Börnstein, "Tabellen"; Seidell, "Solubilities of Inorganic and Organic Compounds"). (It would

TABLE V.

	%		%		%
Ethyl ether	7·0	*iso*Butyric acid ...	55·4	Diethyl ketone ...	4·6
Ethyl acetate ...	8·5	Methyl propionate	5·0	Acetylacetone ...	14·0
Acetic anhydride	12·0	Ethyl acetate	8·5	*n*-Valeric acid ...	3·4
*iso*Butyl alcohol	9·0	Propyl formate ...	2·1	*iso*Butyl formate	1·0
sec.- ,, ,,	22·5	*n*-Butaldehyde ...	3·6	Ethyl propionate	1·7
Trimethylcarbinol	misc.	*iso*Butaldehyde ...	10·0	Propionyl acetate	1·7
n-Butyric acid ...	misc.	Methyl ethyl ketone	24·0		

perhaps have been better to consider critical solution temperatures rather than solubility at a fixed arbitrary temperature, but very few data exist.)

The carboxyl group is by far the most effective in promoting solubility in water; of the two butyric acids, one is completely miscible and the other has very great solubility (the C.S.T. of *iso*butyric acid is 24°). The carbonyl group is next in order of efficacy whether in ketones or in aldehydes, and the hydroxyl group appears to have almost the same effect (possibly a little less) if *compounds containing a similar structure in the remainder of the* molecule are compared, *e.g.*, *iso*butaldehyde with *iso*butyl alcohol, or methyl ethyl ketone with *sec.*-butyl alcohol. Ethereal oxygen has less effect than the hydroxyl group. It is unfortunate that we have no data for methyl propyl ether, for the position of the active group exercises a great influence on the solubility. Thus, we can arrange these groups in the order of their effect on the solubility in water as $CO_2H > CO > CH_2{\cdot}OH, CH{\cdot}OH > {-}O{-}$, there being little difference between CO and OH.

When two or more of these groups are present in the same molecule certain interesting results are obtained. The introduction of the very active carbonyl group into ethyl ether, with formation of ethyl acetate, produces the very small increase of solubility from 7% to 8·5%, and at the same time the dielectric constant is increased only from 4·37 to 5·85. It should be noted that, of the three isomeric esters, ethyl acetate has by far the largest solubility. This seems to afford very distinct evidence of that interaction

between the two oxygen atoms which results in the chemical inactivity of the carbonyl group in esters and produces a contraction in the molecular volume (see above). This effect cannot be explained on the simple electronic theory if the octet rule is inviolable.

On the introduction of a further carbonyl group, with formation of acetic anhydride, a marked increase in solubility is produced (8·5 to 12%), and the dielectric constant is increased from 5·85 to 20·5. In discussing this in relation to the parachor value for acetic anhydride (p. 1195), it was concluded that the results were consistent with the view that one carbonyl group was present and also an ester group. This view seems to be supported by the above data; but it must be pointed out that the solubility is still markedly less than that of a compound, such as methyl ethyl ketone, which contains only one carbonyl group, and also that acetylacetone, in which the two carbonyl groups are separated by a CH_2 group, in spite of its containing one more carbon atom in the molecule, has a greater solubility (14%) than the anhydride and also a higher dielectric constant (23·0). This is remarkable when one considers the very large diminution in solubility produced by one additional carbon atom in the molecule (compare, *e.g.*, diethyl ketone and methyl ethyl ketone, *n*-valeric acid and *n*-butyric acid, Table V).

One must conclude that there is marked conjugation between the three oxygen atoms in the molecule of acetic anhydride, a result which is in agreement with the fact that this substance does not behave chemically as if there were a free carbonyl group present. The insensitiveness of a physical property such as the parachor to structural changes which would have large effects on properties such as solubility or chemical reactivity is well known, *e.g.*, the marked difference in solubility of the isomeric butyl alcohols or C_4 esters which possess the same parachor, or the identity in value for the double bond whether it is conjugated or not, as in ethylene and benzene.

On the introduction of a carbonyl group contiguous to a hydroxyl group, *e.g.*, *iso*butyl alcohol⟶*iso*butyric acid, *n*-butyl alcohol⟶ *n*-butyric acid, an extremely large increase of solubility occurs. The resulting carboxyl group produces a much greater increase in solubility than does a single carbonyl group alone. (The corresponding decrease in dielectric constant is undoubtedly due to the fact that association into dimeric molecules occurs in the absence of water.) On the other hand, that some mutual interaction does occur between these groups is supported by the marked difference in solubility between valeric acid (3·4%) and acetylacetone (14%), both C_5 compounds. This large solubility of the acids in water would seem to be opposed to the view that the single carboxyl

group is a four-membered chelate ring. On the other hand, it does not give much support to the view that the non-reactivity of the carhonyl group in acids and esters is due to the same cause.

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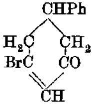
CLII.—*Conversion of Hydroaromatic into Aromatic Compounds. Part II. Action of Bromine on 5-Chloro- and 5-Bromo-1-phenyl-Δ^4-*cyclo*hexen-3-one.*

By Leonard Eric Hinkel and Donald Holroyde Hey.

When chlorine acts on 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one, chlorinated hydroaromatic compounds result which can readily be transformed into aromatic compounds by simple means (Hinkel, J., 1924, **125**, 1847). The present investigation was undertaken not only to obtain analogous halogen compounds of diphenyl, but also to study the influence of the phenyl group in substituted dihydroresorcinols and their derivatives.

As in the case mentioned above, bromine is rapidly absorbed by 5-*bromo*-1-*phenyl*-Δ^4-cyclo*hexen*-3-*one* (I), but, in marked contrast with the behaviour of 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one, 4 : 5 : 5-*tribromo*-1-*phenyl*cyclo*hexan*-3-*one* can he readily isolated in the solid state. This tribromo-ketone exists in two crystalline forms, which probably have the *cis*- and *trans*-configurations (II) and (III); one form is much less stable than the other and from a study of its decomposition would seem to have the structure (III).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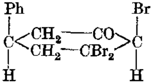
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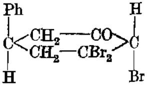
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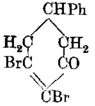
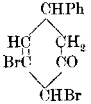
The two forms are readily interconvertible by crystallisation from either absolute alcohol or ether, the latter solvent giving rise to the unstable form. This form loses hydrogen bromide at room temperature when kept for a few days (especially in ethereal solution); the more stable form requires several weeks before showing any appreciable decomposition. The same decomposition can be readily accomplished by heating the tribromo-ketone, either alone or with alcoholic potash. In every case the product of the decomposition

consists of a mixture containing 5-*bromo*-3-*hydroxydiphenyl*, 4 : 5-*dibromo-3-hydroxydiphenyl*, and a small quantity of phenyldihydroresorcinol. Since the positions occupied by the bromine atoms in the tribromo-ketone are known, there can be little doubt that the diphenyl derivatives obtained from it have the structures assigned to them. Experiments are, however, in progress with the object of preparing these compounds synthetically.

The removal of hydrogen bromide from 4 : 5 : 5-tribromo-1-phenyl-*cyclo*hexan-3-one can occur in one of two ways to form the dibromohexenone (IV) or (V). Unlike the corresponding chloro-derivatives

(IV.)   (V.)

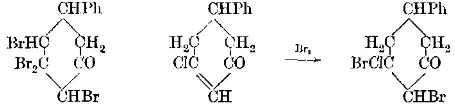
of dimethyldihydroresorcinol (Hinkel, *loc. cit.*), the intermediate dihalogen compound (V) cannot be isolated, it being immediately transformed into 5-bromo-3-hydroxydiphenyl, nor can the dibromohexenone (IV) be obtained from 4-bromo-1-phenyldihydroresorcinol (compare Crossley and Le Sueur, J., 1903, **83**, 110). As the compound (IV) could not give rise to 5-bromo-3-hydroxydiphenyl without undergoing an exceptionally drastic internal rearrangement, it seems probable that the loss of hydrogen bromide occurs at carbon atoms 5 and 6 of the tribromo-ketone, giving the compound (V) (compare Hinkel, *loc. cit.*), from which, by loss of hydrogen bromide from carbon atoms 1 and 4, 5-bromo-3-hydroxydiphenyl can readily be formed.

The presence of 4 : 5-dibromo-3-hydroxydiphenyl among the products of the decomposition of the tribromo-ketone is explained in the following way. A constant product of the decomposition is phenyldihydroresorcinol, which must owe its origin to the presence of some 5-bromo-1-phenyl-Δ^4-*cyclo*hexen-3-one (I) (this is readily hydrolysed to phenyldihydroresorcinol even by the moisture of the air; compare Boyd, Clifford, and Probert, J., 1920, **117**, 1385). It would seem, therefore, that the tribromo-ketone decomposes to a small extent in yet a third manner, giving rise to 5-bromo-1-phenyl-Δ^4-*cyclo*hexen-3-one by loss of bromine. This bromine combines with (V), giving an unstable tetrabromo-compound (VI) (compare Hinkel, *loc. cit.*), which can give 4 : 5-dibromo-3-hydroxydiphenyl by loss of hydrogen bromide.

When the decomposition of the tribromo-ketone is effected by means of alcoholic potash, the yield of hydroxydiphenyl derivatives is diminished owing to the formation of a small quantity of 5-*bromo*-

3-*ethoxydiphenyl* (compare Crossley and Renouf, J., 1914, **105**, 167); 4 : 5-dibromo-3-ethoxydiphenyl is never produced under these conditions. (When a mixture of 5-bromo-3-hydroxydiphenyl and 4 : 5-dibromo-3-hydroxydiphenyl is treated with an alcoholic solution of hydrogen chloride, it is again only the monobromo-derivative which yields an ethoxy-compound.)

The action of bromine on 5-chloro-1-phenyl-Δ^4-*cyclo*hexen-3-one (VII) gives rise to 5-*chloro*-4 : 5-*dibromo*-1-*phenyl*cyclo*hexan*-3-*one* (VIII), which resembles the tribromo-analogue in existing in a stable and an unstable form. In its decomposition with alcoholic potash, however, it yields a monobromo- and a monochloro-hydroxy-



(VI.) (VII.) (VIII.)

diphenyl in molecular proportion, in addition to a mixture of dihalogen derivatives. The monohalogen compounds were identified through their ethoxy-derivatives. This result is in marked contrast with the behaviour of other chlorobromo-hydroaromatic compounds, from which liberation of hydrogen bromide always precedes that of hydrogen chloride (compare Crossley, J., 1904, **85**, 264).

EXPERIMENTAL.

5-*Bromo*-1-*phenyl*-Δ^4-cyclo*hexen*-3-*one* (I).—30 G. of phenyldihydroresorcinol (2 mols.) were suspended in 100 c.c. of dry chloroform and heated at 70° for 3 hours with 25 g. of phosphorus tribromide (excess of 1 mol.); the chloroform was then evaporated. The residue was poured into water and extracted three times with ether. From the extracts, washed with 4% sodium hydroxide solution and with water and dried over calcium chloride, a substance was obtained which crystallised from alcohol in transparent, colourless plates, m. p. 81·5° (Found: Br, 31·6. $C_{12}H_{11}OBr$ requires Br, 31·9%). The *ketone* has an irritating effect on the skin, and when kept in a moist atmosphere gradually reverts to phenyldihydroresorcinol with liberation of hydrogen bromide.

4 : 5 : 5-*Tribromo*-1-*phenyl*cyclo*hexan*-3-*one*.—6·4 G. of bromine (1 mol.), dissolved in 22 c.c. of chloroform, were added to a well-cooled solution of 10 g. of 5-bromo-1-phenyl-Δ^4-*cyclo*hexen-3-one (1 mol.) in 30 c.c. of chloroform; rapid absorption of the bromine soon occurred, with rise in temperature. The chloroform was evaporated in a current of dry air at room temperature and the solid

residue was dissolved in warm alcohol, from which it crystallised in sheaves of large, white needles, m. p. 82° (decomp.) (Found: Br, 58·2. $C_{12}H_{11}OBr_3$ requires Br, 58·4%). The needles can be kept in a dry atmosphere for several weeks without suffering much decomposition. Crystallisation from ether gives transparent prisms, which also melt at 82°, and show appreciable decomposition with liberation of hydrogen bromide after being kept for 1 day.

Action of heat. 12 G. of the tribromo-ketone were gently heated on the water-bath until the evolution of hydrogen bromide ceased. The dark semi-solid product was triturated with ether and the small quantity of phenyldihydroresorcinol which separated was removed by filtration. The filtrate on evaporation left a brown, oily residue, which was dissolved in light petroleum (b. p. 40—60°). After slow evaporation in the cold, the solution deposited white crystals. These were separated from the liquid (filtrate A), washed with light petroleum, and recrystallised from that solvent, 4 : 5-*dibromo-3-hydroxydiphenyl* separating in clusters of small, white needles, m. p. 81° (Found: Br, 48·7. $C_{12}H_8OBr_2$ requires Br, 48·8%). The *benzoyl* derivative, formed in the usual manner, crystallised from alcohol in small, white needles, m. p. 104° (Found: Br, 36·9. $C_{19}H_{12}O_2Br_2$ requires Br, 37·0%).

Filtrate A. The light petroleum was removed by evaporation, and the residual oil distilled in a vacuum, 5-*bromo-3-hydroxydiphenyl* being obtained as a colourless oil, b. p. 208—210°/11 mm. (Found: Br, 31·9. $C_{12}H_9OBr$ requires Br, 32·1%). The *benzoyl* derivative crystallised from alcohol in clusters of small needles, m. p. 108° (Found: Br, 22·85. $C_{19}H_{13}O_2Br$ requires Br, 22·7%).

Action of alcoholic potassium hydroxide. A 20% solution of potassium hydroxide was gradually added to an alcoholic solution of 20 g. of the tribromo-ketone, until the supernatant liquid remained alkaline after being gently warmed on the water-bath for a few minutes. Most of the alcohol was then removed by warming under diminished pressure, and the mixture was diluted with water, acidified, and shaken with ether, which extracted a dark liquid only partly soluble in aqueous sodium hydroxide. The insoluble portion was crystallised from alcohol, 5-*bromo-3-ethoxydiphenyl* separating in white clusters, m. p. 70—71° (Found: Br, 28·7. $C_{14}H_{13}OBr$ requires Br, 28·9%). This compound can also be obtained by warming an alcoholic solution of 5-bromo-3-hydroxydiphenyl in presence of hydrogen chloride. As 4 : 5-dibromo-3-hydroxydiphenyl does not readily form an ethoxy-derivative under similar conditions, this serves as a convenient method for the separation of the two hydroxy-derivatives.

The alkaline filtrate from 5-bromo-3-ethoxydiphenyl was acidified,

and ether then extracted a brown viscous oil, which consisted of a mixture of 5-bromo-3-hydroxydiphenyl and 4 : 5-dibromo-3-hydroxydiphenyl, the separation of which was effected with light petroleum as described above.

5-Chloro-4 : 5-dibromo-1-phenylcyclohexan-3-one (VIII).—20 G. (1 mol.) of 5-chloro-1-phenyl-Δ^4-*cyclo*hexen-3-one (Boyd, Clifford, and Probert, J., 1920, **117**, 1383) in 40 c.c. of chloroform were brominated with 16 g. of bromine (1 mol.) in 50 c.c. of chloroform under the conditions described on p. 1202. The product crystallised from warm alcohol in semi-opaque, prismatic crystals, m. p. 98·5° (Found: Br, 43·5; Cl, 9·3. $C_{12}H_{11}OClBr_2$ requires Br, 43·7; Cl, 9·7%). When crystallised from alcohol, the compound is comparatively stable and can be kept for several weeks in a dry atmosphere. It crystallises from ether in transparent, rhombic crystals, m. p. 88·5°, which evolve hydrogen bromide gradually at room temperature and rapidly when warmed. They can be reconverted into the stable variety by crystallisation from alcohol.

Action of alcoholic potassium hydroxide. The reaction was carried out as described on p. 1203 and yielded a liquid product a portion of which was insoluble in aqueous sodium hydroxide. This portion crystallised from alcohol in clusters of small, white needles, m. p. 68—69°, and consisted of a mixture of 5-*chloro*- and 5-*bromo*-3-*ethoxydiphenyl* in molecular proportion (Found: Br, 15·7; Cl, 7·0. A molecular mixture of $C_{14}H_{13}OBr$ and $C_{14}H_{13}OCl$ requires Br, 15·7; Cl, 7·0%). The alkaline solution containing 5-chloro- and 5-bromo-3-hydroxydiphenyl, in addition to dihalogenohydroxydiphenyls, was not further examined.

UNIVERSITY COLLEGE, SWANSEA. [*Received, February 24th,* 1928.]

CLIII.—*The Inhibition of Esterification by Pyridine.*

By KENNETH CLAUDE BAILEY.

THE velocity of reaction of ethyl alcohol and acetic acid to form ethyl acetate and water is diminished by the addition of minute quantities of pyridine, the diminution being marked even with 3 parts (by volume) of pyridine per million parts of solution. Under the experimental conditions employed, an esterification of 3·1% in 6 hours, in the absence of any negative catalyst, was reduced to about 1·7% by addition of about 70 parts of pyridine per million; but further addition (up to 800 parts per million) only reduced esterification to 1·37%.

These results seem to indicate that the reaction takes place in two ways, probably (*a*) in the body of the liquid, and (*b*) on the surface of the containing vessel. If one assumes that the surface reaction is more likely to be inhibited by small traces of a negative catalyst—an assumption justified by the data given later—the results snggest that esterification takes place in manner (*a*) to the extent of about 1·7%, and in manner (*b*) to the extent of about 1·4%.

The effective surface was increased by the insertion of glass tubes, the total surface area of which was approximately the same as that of the vessel. Esterification, in the absence of pyridine, now reached 4·7%, the increase of 1·6% being ascribed to the increased surface. By addition of about 300 parts of pyridine per million the esterification was once more reduced to 1·7%, the addition of further pyridine having comparatively little effect.

The glass surface possesses, no doubt, a limited number of active points at which reaction takes place. These can be preoccupied by pyridine molecules, even when the concentration of pyridine in the body of the liquid is small. The effect of pyridine on the liquid reaction depends, however, on its absolute concentration, and is therefore small unless the concentration of pyridine is considerable. With increased surface, a greater amount of pyridine is necessary to saturate the active points, but the extent of liquid reaction, after the surface reaction has been eliminated, is approximately the same.

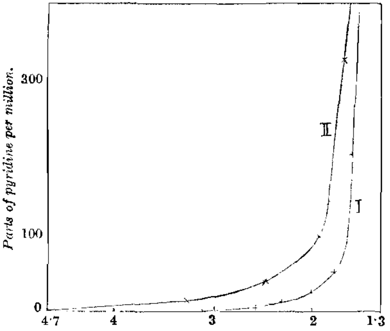
Experiments are being carried out with a view to elucidate the mechanism by which the surface reaction is inhibited by pyridine.

EXPERIMENTAL.

The physical constants of the reagents employed were as follows: Ethyl alcohol, *d* 0·794 (99%); acetic acid, redistilled, b. p. 116—118°; pyridine, dried with potassium hydroxide and distilled, b. p. 114°. Three mols. of ethyl alcohol were used to one mol. of acetic acid.

The duration of each experiment was six hours, during which the temperature could be accurately controlled, and the temperature coefficient was determined. The vessel employed (volume about 110 c.c.; surface area about 112 sq. cm.) was approximately spherical, with a ground glass stopper which fitted closely, but permitted the escape of vapour as the liquid expanded. The vessel was thus always completely, or almost completely, full of liquid. In the following tables the esterification is given as percentages of

acetic acid esterified, and the concentration of pyridine as parts per million parts of solution.



Change of velocity with temperature (no catalyst).

Temperature	31·9°	33·1°	39·6°	41·6°	44·1°	47·7°
Esterification, % ...	1·70	1·98	2·67	2·84	3·16	4·11

A curve was drawn, from which the results of subsequent experiments were corrected for small variations of temperature.

Effect of addition of pyridine (Curve I); temperature 43°.

Conc. of pyridine ...	Nil	3	8	11	24	50	200	800
Esterification, % ...	3·12	2·57	2·41	2·31	2·09	1·78	1·60	1·37

A second series of similar experiments, carried out with different specimens of alcohol and acid, gave a curve almost identical with Curve I, thus:

Conc. of pyridine	Nil	16	40	80	400
Esterification, %	3·12	1·72	1·57	1·57	1·33

Effect of increasing the glass surface (Curve II).

Eight small glass tubes (total surface area about 112 sq. cm.) were inserted, to double the effective surface area of the vessel.

Conc. of pyridine	Nil	13	38	96	320
Esterification, %	4·70	3·28	2·49	1·94	1·69

The author wishes to express his thanks to Mr. W. E. Lewis, B.A., by whom some preliminary experiments were performed.

TRINITY COLLEGE, DUBLIN. [*Received, March 20th,* 1928.]

CLIV.—*Some Experiments on Intensive Drying.*

By Ronald Herbert Purcell.

1. *The Influence of Drying on the Reduction of Copper and Bismuth Oxides by Carbon Monoxide.*

Much work has been done on the reduction of metallic oxides by carbon monoxide and hydrogen (Jones and Taylor, *J. Physical Chem.*, 1923, **27**, 623), but the effect of removing the last traces of water from the reactants has not previously been demonstrated. In the present paper the effect of drying on the reduction of copper, bismuth, mercury, and silver oxides by carbon monoxide is described; the influence of introducing a small quantity of dry impurity has been investigated in the case of copper oxide; and lastly, the reduction of copper oxide by hydrogen has been examined.

The carbon monoxide was prepared by the interaction of pure redistilled formic and sulphuric acids in an all-glass apparatus, which was a modified form of that used by Tramm (*Z. physikal. Chem.*, 1923, **105**, 356). The gas was washed by two cylinders of alkaline pyrogallol, and then partially dried by pure sulphuric acid. All glass apparatus used was cleaned by filling with nitric–chromic acid mixture which was kept hot for 12 hours. After standing for a further 12 hours, the apparatus was washed out with distilled water, and steam, generated in an all-glass apparatus from distilled water, was passed for 2 hours. Finally, the apparatus was washed with conductivity water and dried in a current of dry air.

The copper oxide was prepared by oxidising pure copper foil in a current of carbon dioxide-free air, the copper being heated to redness in an electric furnace, and precautions being taken to prevent any contamination from the walls of the silica furnace. After being powdered in an agate mortar, the oxide was dried in an apparatus made from Jena combustion glass (Fig. 1), 0·2 g. being placed in each of the side tubes *b*, and the apparatus connected *via* a mercury trap to the vacuum pumps. These, which were used throughout the research, consisted of a Vitreosil mercury-vapour pump and a Hyvac oil-pump. After a preliminary evacuation, some pure phosphoric oxide, sublimed in oxygen at 200° and therefore crystalline and not powdery, was introduced into the side tube *C*, which was at once resealed. The pumps were again started and, apart from the phosphoric oxide compartment, all glass parts were thoroughly baked out. The apparatus was sealed off at the constriction *a*, and the side tubes were placed in an oven where they were continuously heated at 450°, the phosphoric oxide compartment being meanwhile cooled in water. When dry, the bulbs of copper oxide were drawn

off at the constrictions (c', c'') and sealed into tubes of the form shown in Fig. 2, which could be filled with carbon monoxide. The tubes were cleaned, dried, and connected to the carbon monoxide generator and the pumps. After a preliminary evacuation the apparatus was filled with gas. The end of the tube (C) was cut off and, after the introduction of some pure phosphoric oxide, immedi-

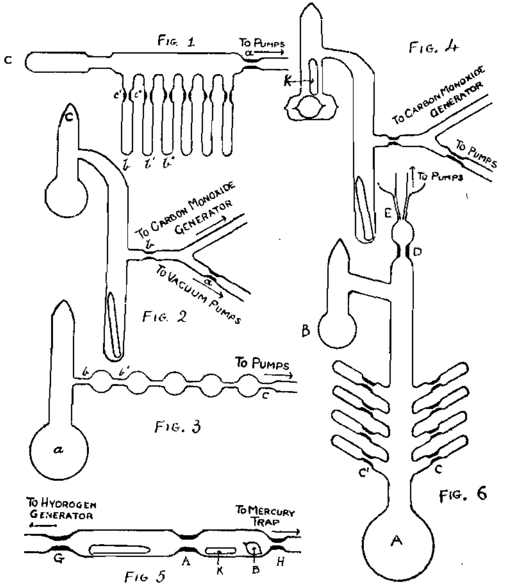


FIG. 1. FIG. 2. FIG. 3. FIG. 4. FIG. 5. FIG. 6.

ately resealed. The tube was baked out under vacuum, filled with carbon monoxide, and again evacuated. The pumps were sealed off at the capillary a, and the tube was filled with carbon monoxide to 60 cm. pressure. It was sealed off at b, and heated at 400°, the phosphorus pentoxide compartment being meanwhile cooled. In order to examine a tube, the bulb of oxide was broken by allowing it to fall on to the bottom of the tube, the pentoxide compartment

being held below the reaction tube so that none of the drying agent was thrown on the copper oxide. The reduction was followed by the change in colour of the oxide, and since the carbon monoxide was always in excess a mass of red copper was the final product.

Comparison tubes were made in which the phosphoric oxide was omitted. In these the copper oxide was completely reduced by heating at 100° for 90 minutes or at 150° for 10 minutes. When the dry tubes were examined it was found that the temperature required for reaction increased with the time of drying, until a maximum was reached, beyond which further periods of drying had no effect. For instance, after the copper oxide had been dried for 10 days and the carbon monoxide for 7 days, the copper oxide was only reduced after 20 hours at 100° and 90 minutes at 180°. When both the reactants had been dried for a month, reduction would only take place at 425°, and was then complete in 15 minutes. Tubes have been examined in which the carbon monoxide has been dried for 18 months and the copper oxide for 6 months, but the oxide was always reduced at about 425°.

The above experiments were repeated under the same conditions with pure bismuth oxide. In the undried comparison tubes the reduction was complete in $2\frac{1}{2}$ hours at 175° and in a few minutes at 250°. Again it was found that drying decreased the rate of reaction and that the temperature required for reduction increased to a maximum at 430° after 10 weeks' drying.

There are two possible explanations of the above results. Either the oxides react with carbon monoxide at 430° in the absence of water, or appreciable amounts of water are given off by the glass or copper oxide at that temperature. It is possible that the dry carbon monoxide is decomposed into carbon dioxide and carbon on the surface of the oxide, and reduction is effected by the carbon so deposited, since carbon monoxide is known to be decomposed on catalytic surfaces at considerably lower temperatures (Cleminson and Briscoe, J., 1926, 2148). The liberation of water from such a hard glass is improbable at this relatively low temperature, especially in view of the fact that increases in the temperature to which the tubes were heated during drying did not affect the temperature required for reduction.

2. *The Reduction of Mercuric and Silver Oxides by Carbon Monoxide.*

The mercuric oxide was prepared from the metal (purified by prolonged agitation with dilute nitric acid and then thrice distilled) by heating it at 425° in a hard-glass tube with oxygen, which was drawn from a cylinder, passed through a soda-lime tube and a cotton-wool filter, and maintained at 5 atmos. pressure. After a

week's heating, the mercuric oxide formed was removed and ground in an agate mortar, any free mercury being removed by heating to 360° in a stream of oxygen.

The oxide was dried in the usual glass apparatus, which was then evacuated, all glass parts being baked out when possible. After sealing off from the pumps, attempts were made to dry the oxide by maintaining it at temperatures between 100° and 300°. When it was thought to be dry, the side tubes were drawn off and sealed into outer tubes which were filled with carbon monoxide. In comparison tubes, from which the phosphoric oxide was omitted, it was found that reduction was rapid at 180°, and this temperature was therefore chosen for examining the dry tubes. Although the oxide was dried for periods of up to 8 months and the gas for one year, in no case was any appreciable difference observed between the dry tube and the damp comparison tube that was heated with it.

Silver oxide was prepared by mixing equimolecular solutions of recrystallised baryta and silver nitrate in conductivity water. The precipitate was rapidly filtered off, washed with conductivity water, and dried over phosphoric oxide in a desiccator. The oxide obtained was reduced by carbon monoxide within 30 minutes at room temperature. Small amounts of it were placed in tbe usual drying tubes, which were exhausted with cautious heating. Attempts were made to dry the oxide by keeping it for as long as 18 months at 15°, 100°, or 200°, and the bulbs were then sealed into outer tubes in which the carbon monoxide was dried for as much as 6 months. Again, however, it was impossible to detect any change in the rate of reduction on drying.

3. *The Influence of a Dry Third Substance on the Reduction of Copper Oxide by Carbon Monoxide.*

It is of importance to determine how far other substances can act as catalysts in the absence of water, and an attempt has been made to test this in the above reaction, the effect of introducing small amounts of sulphur dioxide, bromine, ether, alcohol, or benzene being observed.

These substances were dried in the apparatus shown in Fig. 3. Some pure phosphoric oxide was placed in bulb *a*, and some of it was sublimed in a stream of dry oxygen into each of the small bulbs. The liquids used were samples of pure materials that had been previously used in intensive-drying experiments. A small quantity was placed in the flask and the neck was sealed off. The apparatus was exhausted while the liquid was cooled in a freezing mixture. After sealing off at *C* from the pumps, the bulbs were sealed off at the capillaries (*b*, *b'*), so that they contained about 2 c.c. of the

vapour. With sulphur dioxide, the bulbs were alternately exhausted and filled with gas, and then sealed off so that they contained about 1 c.c. of gas at N.T.P. After drying for about 2 months, the bulbs were sealed into outer tubes as shown in Fig. 4, a bulb of dry copper oxide being placed in the other limb.

The tubes were cleaned and filled with carbon monoxide, the phosphoric oxide being placed in the compartment with the foreign substance. Ten tubes were thus prepared, two for each substance. After drying, the bulbs were broken by the weight *K* and the copper oxide bulb by shaking. The copper oxide in the tubes was then heated at 100° for 24 hours without reduction occurring. There was also no change on heating for 6 hours at 175°, but after 30 minutes at 225°, the oxide in those tubes containing alcohol, ether, and benzene was reduced. The tubes containing sulphur dioxide and bromine were heated without change for 30 minutes at 275°, 325°, and 375°, but at 425° the oxide was reduced in each case. Thus sulphur dioxide and bromine have no power to act in the place of water in this reaction, and the organic vapours appear to catalyse it, though not so efficiently as water. Two possibilities have to be considered; the liquids may begin to undergo incipient decomposition with the copper oxide, or they may have been insufficiently dried, the water introduced with them making the reaction appreciably rapid at 225°.

4. *The Reduction of Copper Oxide by Hydrogen.*

The hydrogen was prepared by electrolysis of a solution of baryta that had been recrystallised ten times and was free from chloride. It was found that the best form of electrolytic vessel was a U-tube with platinum electrodes let in from the top, so that the tube could be cooled by water on the outside. The hydrogen was passed over red-hot copper gauze and dried with phosphoric oxide, the gas flow being controlled by a mercury-sealed tap lubricated with phosphoric acid. The copper oxide was dried as previously described, and was sealed into tubes of the form shown in Fig. 5.

This apparatus was connected to the hydrogen generator through a mercury-sealed ground glass joint. A mercury trap and a phosphoric oxide tube prevented air diffusing back. The hydrogen was passed for 4 hours, the glass walls being meanwhile heated. The tube was sealed off while warm at the capillaries *G* and *H*, so that the gas was under slightly reduced pressure on cooling. The bulb of phosphoric oxide, *B*, was broken by the breaker, *K*, and the compartment containing the copper oxide bulb was kept at 400°. When a tube was thought to be dry, it was separated at the constriction *A*, and the bulb of copper oxide broken. It was then

heated together with an undried comparison tube. With periods of drying up to 2 years no differences have been observed in the time of reduction of the damp and the dried materials.

5. *A Quantitative Study of the Reduction of Copper Oxide by Carbon Monoxide.*

In the previous experiments the reaction could only be approximately followed by the colour change or by estimation of the carbon dioxide formed after heating for a certain time. Further information was required about the speed of the reaction when it had been materially diminished by drying. This was obtained by passing a stream of dry carbon monoxide over the dry copper oxide and analysing the issuing gas which was collected in 10 c.c. samples. The amount of carbon dioxide in any one sample was regarded as proportional to the mean speed of reaction in the interval while that sample was being collected. An elaboration of the apparatus used by Baker for the combustion of carbon in oxygen was employed for this purpose (*Proc. Roy. Soc.*, 1888, **45**, 1). The carbon monoxide was stored over concentrated sulphuric acid and the gas from this reservoir displaced that from a large flask where it had been dried over phosphoric oxide. This dry gas displaced the intensively dried gas in a second and a third bulb. After passing through a mercury trap to prevent diffusion back into the bulb, it was passed over 1 g. of copper oxide in a boat that could be heated in an electric furnace. A small pump ensured regular flow of the gas, and the mercury valve of this also prevented water vapour diffusing back to the copper oxide. The copper oxide was dried *in situ* by heating to 400° in a vacuum with a phosphoric oxide tube attached.

If the copper oxide were not intensively dried a normal reduction curve was observed. This can be divided into a short period of induction when little or no carbon dioxide is formed, a period when the reduction proceeds at a rapidly increasing rate, and finally a decrease as all the copper oxide becomes reduced. When the reactants were dried, the amount of carbon dioxide formed was much less and it did not become greater with the time. Table I shows the amounts of carbon dioxide found in the issuing gas at the

TABLE I.

Temperature of Oxide, 150°.

Time	90	120	150	195	240	270
CO_2 %	0·5	0·5	0·4	0·6	0·4	0·4

Temperature increased to 196°.

Time	330	350	360	371	410	480
CO_2 %	4·4	4·4	5·0	5·5	5·6	4·5

given time (in minutes from the beginning of the experiment), the reactants having been dried for 7 days. Table II shows the normal curve obtained with the same sample of oxide.

TABLE II.

Temperature of Oxide, 150° (undried).

Time	9	15	30	42	60	87	101
CO_2, %	0·1	0·5	1·4	3·0	9·0	17·0	25·0

Table III gives the constant percentages of carbon dioxide obtained in comparable experiments at different temperatures. The period of drying was in each case one week and the same sample of oxide was used.

TABLE III.

CO_2, %	0·4	0·6	3·0	5·0
Temp. of CuO	150°	160°	180°	195°

Thus it is shown that with the dried reactants the speed of reduction depends on the temperature and the amount of water present. The copper formed does not appear to catalyse the reaction when there is only a very little water vapour present, although it does so when the system has not been dried (Jones and Taylor, *loc. cit.*).

6. *The Effect of Intensive Drying on the Union of Mercury and Oxygen.*

Although mercury can be obtained in a pure state and its physical properties are changed by drying (Baker, J., 1922, **121**, 568), it has not been possible to change its chemical reactivity. Similar negative results have been obtained with some of its compounds; for instance, Baker has found that mercuric oxide decomposes at a normal rate after 20 years' drying, and, as shown earlier, dry mercuric oxide and carbon monoxide reacted normally. Consequently, an attempt was made to observe any change in the rate of formation of the oxide from its elements.

The mercury was purified as previously described and 50 c.c. were placed in the bulb *A* of the apparatus shown in Fig. 6. Some pure phosphoric oxide was introduced into the side tube *B*, which was at once sealed off. The apparatus was baked out under vacuum and then sealed off at the constriction *D*. During the period of drying the mercury in *A* was heated so that it continuously distilled and condensed in the upper part of the tube. Samples of the dry mercury were sealed off in the side tubes *C*, *C'*, and these were sealed into larger tubes similar to those shown in Fig. 5.

The oxygen was prepared by the electrolysis of baryta in an apparatus like that employed for hydrogen. Traces of hydrogen

were removed by passage over red-hot copper oxide. The gas was roughly dried by a flask containing concentrated sulphuric acid, and the flow controlled by a mercury-sealed tap lubricated with phosphoric acid.

The tube to be filled was connected to the vacuum pumps and to the oxygen generator *via* a glass diaphragm that could be broken when required. Pure phosphoric oxide was placed in its compartment, which was then sealed off. The tube was baked out in a vacuum, the pumps were sealed off and, after the diaphragm had been broken, filled with oxygen to a little below atmospheric pressure, and the tube was sealed off and heated to 450° to accelerate drying, the phosphoric oxide compartment being meanwhile cooled. After 10 days' heating, the drying of the tube was continued at room temperature. Each tube was examined by drawing off the phosphoric oxide bulb and breaking the tube of mercury; it was then heated together with a damp comparison tube at 400° for 30 minutes and the amounts of oxide formed were compared. Even after 6 months' drying it has not been possible to detect any difference in the rate of formation of the oxide.

Water has been shown to be necessary for a great variety of chemical reactions (H. B. Baker, J., 1894, **65**, 622, *et seq.*), but it is not known what reactions, if any, take place in the absence of water, for failure to observe any change in the velocity of reaction may equally well be ascribed to imperfections in technique. In considering the above results, one is justified in assuming that mercuric oxide is formed from its elements and reacts with carbon monoxide while in a very dry state. It is, however, incorrect to assume that, because a substance is " dry " with respect to one reaction, there is not enough water there for another to proceed normally. This is known not to be the case. For example, carbon monoxide does not explode with oxygen after passing through sulphuric acid, yet a month's drying over phosphoric oxide is necessary to prevent its reducing copper oxide. Also, although Coehn and Tramm have found that samples of hydrogen and oxygen, which did not explode on heating, combined at a normal rate in ultra-violet light, yet Baker and Carlton (J., 1925, **127**, 1990) have shown that the photochemical combination can be influenced by drying. The accumulation of negative results for mercury and its compounds does, however, indicate that they can react in the presence of unusually small amounts of water, a result which is being tested by still further experiments.

The author wishes to express his sincere gratitude to Professor H. B. Baker, under whose direction these experiments were carried

out; also to thank the Board of Scientific and Industrial Research for a maintenance grant, and Messrs. Brunner Mond, Ltd., out of whose grant some of the apparatus was bought.

ROYAL COLLEGE OF SCIENCE,
LONDON, S.W. 7. [*Received, February 28th*, 1928.]

CLV.—*The Determination of Volatile Matter in Coke.*

By FREDERICK JOHN EATON and STUART PEXTON.

DURING certain investigations upon the reactivity of coke it was found necessary to determine accurately the content of volatile matter. The method of the American Society of Testing Materials (1924, D, 37, 1018) and a method adapted from the Bone and Silver method for coals (J., 1921, **119**, 1145) were examined. In the former method the coke, in a platinum crucible, is heated in an electric furnace at 950° (Fieldner, U.S. Bureau of Mines, Tech. Paper No. 76), but no special precautions are taken to prevent losses in weight due to oxidation, although Fieldner (*ibid.*, p. 20) states that when the same method is used for coal, where oxidation is minimised by the presence of a reducing atmosphere in the crucible, oxidation losses amount to less than 0·3%. In the adapted Bone and Silver method, coke is heated in a silica tube filled with nitrogen until evolution of gas ceases; a disadvantage of this method is that, owing to the low conductivity of silica, the test is prolonged and the final temperature of the coke uncertain.

The following method has been found to combine the rapidity of the first method with the trustworthiness of the second.

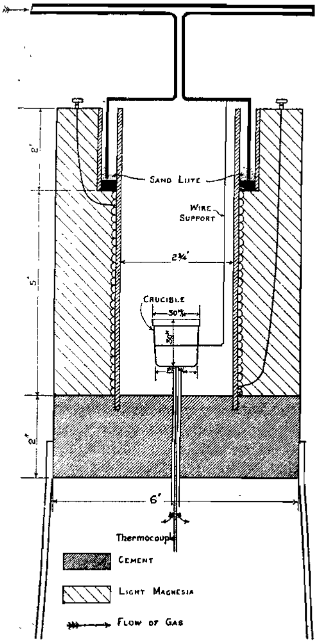
Apparatus.—The apparatus is shown in section in Fig. 1. The platinum crucible is suspended by nichrome wire from a monel metal cap, so that when in position in the electric furnace the thermocouple junction touches the base of the crucible. Nitrogen is fed at a steady rate (200 c.c. per minute) into the furnace through a cap sealed by the sand lute and escapes through the silica tube which carries the thermocouple.

Procedure.—1·1 G. of the sample, ground to pass a 70-mesh sieve (I.M.M. Standard), are weighed into a small test-tube and then dried for 1 hour at 120—130°. After cooling in a desiccator, the coke is weighed in a tared platinum crucible protected from moisture by a porcelain lid, which is used instead of the platinum lid because the weight of the latter, when in the furnace, is affected by particles of sand falling from the lute.

Air is displaced from the furnace tube by a current of nitrogen, and the platinum crucible, closed with a tightly fitting platinum

lid, is introduced into the furnace. The heating current is controlled by an external resistance so that the initial temperature of 950° ± 10° is regained after one minute. After 2 minutes the temperature should be stationary at 950° ± 2°. The temperature

Fig. 1.



is recorded every 10 seconds for the remaining 5 minutes. At the end of 7 minutes the crucible is withdrawn and placed on a slab of brass (to ensure sudden cooling) in a desiccator. When cold the crucible is reweighed with the porcelain lid. The loss in weight

expressed as a percentage by weight of the original coke represents the volatile matter.

If the determination is carried out as directed, the variations in the percentage obtained should not exceed ± 0·05. Particular attention must be paid to the fineness of the sample, prevention of absorption of moisture during weighing, accurate temperature control, and the brightness of the crucible.

The new method possesses the following advantages: (1) Errors due to oxidation are avoided by heating in a current of nitrogen, and it is therefore possible to obtain comparable results with cokes of different reactivities towards oxygen. (2) The temperature of heating is accurately known, since the thermocouple junction is placed close to the base of the platinum crucible. (3) The method is rapid, since the coke is heated in a platinum crucible which has a high heat transmission and low heat capacity, and the coke rapidly attains a temperature of 950°.

The following table gives examples of the results obtained for the percentage of volatile matter.

	Adapted Bone and Silver method:			
Sample.	10 minutes' *heating.*	60 minutes' *heating.*	American *method.*	Authors' *method.*
A	1·37, 1·18, 1·30, 1·67	1·86, 1·71	3·02, 2·92, 2·76, 2·66, 2·58	1·52, 1·55, 1·58, 1·59
B*	1·86, 1·81	2·5, 3·12	7·84, 7·34, 7·52	2·56, 2·5, 2·61
C	1·74, 1·8	2·2, 2·36	3·06, 3·04	1·98, 1·92, 1·92, 1·92
D	0·92, 0·94	1·63, 1·73	4·4, 4·42	1·78, 1·76
E	0·75	0·94, 1·08	2·8, 2·76	1·03, 1·02, 1·06, 1·03

* This sample was a specially reactive coke.

THE GAS LIGHT AND COKE CO.,
LONDON. [*Received, February 29th, 1928.*]

CLVI.—*The Nature of the Alternating Effect in Carbon Chains. Part XXV. The Mechanism of Aromatic Side-chain Substitution.*

By CHRISTOPHER KELK INGOLD and EUGENE ROTHSTEIN.

THE general problem of the influence of nuclear substituents on reactions in side chains attached to an aromatic nucleus is greatly simplified by the assumption that side-chain reactions fall into two main categories, in one of which (type *A*) facilitation occurs by the *influx* of electrons towards, and in the other (type *B*) by a *recession* of electrons from, the side chain concerned. Theoretically,

each of these types requires further subdivision. For instance, the circumstances of the general mechanism *A* would obtain if in the first stage * of reaction a potential anion became ionised or dissociated (type A_1); equally, they would obtain if, in the first stage, a potential (or actual) cation became attracted or co-ordinated (type A_2). Again, the conditions required for mechanism *B* would be present, either if a potential cation were initially ionised or dissociated (type B_1), or if a potential (or actual) anion were initially attracted or co-ordinated (type B_2). As an example, two mechanisms are possible for the hydrolysis (or alcoholysis) of benzyl chloride:

$$C_6H_5\cdot CH_2Cl \begin{cases} \longrightarrow C_6H_5\cdot\overset{+}{C}H_2\}\overset{-}{Cl} \xrightarrow[(H_2O)]{} C_6H_5\cdot CH_2\cdot OH + H\{Cl \text{ (type } A_1) \\ \xrightarrow[(OH')]{} C_6H_5\cdot CH_2 \overset{\textstyle -Cl}{\underset{\textstyle \cdot\cdot OH'}{}} \longrightarrow C_6H_5\cdot CH_2\cdot OH + Cl' \text{ (type } B_2) \end{cases}$$

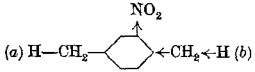
and the probable assumption that the first predominates in neutral or acid solution, whilst the second supervenes in strongly alkaline solution, removes the apparent inconsistency between the results of Franzen and Rosenberg on the alkaline decomposition (*J. pr. Chem.*, 1920, **101**, 333) and those of Olivier and Berger (*Rec. trav. chim.*, 1923, **42**, 775; 1927, **46**, 605) on the acid hydrolysis of benzyl chloride and its nuclear substitution products. Other applications of the above classification of side-chain reactions have been given elsewhere (*Ann. Reports*, 1927, p. 155).

The substitution of halogen, nitroxyl, etc., for a side-chain hydrogen atom might *a priori* belong to either of the two main categories, for substitutions analogous to both types are known in Organic Chemistry. For instance, nuclear aromatic substitution is a process analogous to *A*, since it requires available electrons at the point of reaction: the initial process is to *attract* a potential cation (*e.g.*, entrant Hal or NO_2) and thus the order of facilitation by substituents is $NH_2 > OMe > Me > H$, etc. On the other hand, the α-halogenation of carbonyl compounds is analogous to *B*, since it requires the recession of electrons from the point of substitution: the initial process is to *split off* a cation (*viz.*, H^+) (compare Orton, Hughes, and Watson, J., 1927, 2461), so that the order of facilitation is $COMe > COCl > CO_2H > H$, etc. (compare Ingold, Shoppee, and Thorpe, J., 1926, 1477).

If mechanism *B* (prior ionisation of hydrogen) were to operate in the side-chain halogenation of toluene and similar substances, there are few substituents which would facilitate its action more strongly than an *o*- or a *p*-nitro-group, for *o*- and *p*-nitrotoluenes are

* In the absence of evidence that intermediate products are present in appreciable concentration during the progress of a reaction the first hypothetical stage may be regarded as the rate-determining stage.

known to undergo reactions indicating that their side-chain hydrogen is prone to ionisation; indeed, these compounds even exhibit certain similarities to nitromethane and other pseudo-acids. A *m-nitro-group would also be expected to exert a facilitating action*, but it would be much weaker (Ingold and Shaw, J., 1927, 2918) and, accordingly, the nitro-group in nitro-*p*-xylene (formula below) should orient side-chain substitution in the direction of the group marked (*b*). On the other hand, if the mechanism were of type *A* (*prior attraction of potential cation by electrons), it should be* inhibited very strongly by an *o*- or a *p*-nitro-group, and only to a much smaller extent by a *m*-nitro-group (*ibid.*), and thus in nitro-*p*-xylene predominating substitution should occur in the side-chain marked (*a*):



Furthermore, if mechanisms *A* and *B* operated simultaneously in side-chain substitution of toluene and *p*-xylene, substitution in the nitro-xylene would occur mainly in the group marked (*b*), for the effect of the nitroxyl group is generally to suppress process *A* and facilitate *B*.

We have therefore examined the side-chain bromination of nitro-*p*-xylene and find that side-chain substitution occurs to the extent of at least 76% in the side chain (*a*). We conclude that the side-chain halogenation (and probably also nitration) of alkylbenzenes and their nuclear substitution products proceeds by mechanism *A*; a similar mechanism probably applies to the substitutions of methane and other aliphatic hydrocarbons.

On comparing this conclusion with that which might be derived from the work of Lapworth and Shoesmith on the reverse process, namely, the reduction of substituted benzyl halides (J., 1922, **121**, 1392, and later), mechanisms (all in good agreement with the available data) may be formulated to complete the exemplification of the general classification of side-chain substitutions, already partly illustrated (above) by the hydrolysis of benzyl chloride:

$$C_6H_5{\cdot}CH_3 \longrightarrow C_6H_5{\cdot}CH_3 \cdots \overset{\delta+}{Br}{\cdot}\overset{\delta-}{Br} \longrightarrow C_6H_5{\cdot}CH_2Br + H\{Br \quad (\text{type } A_2)$$

$$C_6H_5{\cdot}CH_2Br \longrightarrow C_6H_5{\cdot}\overset{-}{CH_2}\}\overset{+}{Br} \xrightarrow[(HI)]{} C_6H_5{\cdot}CH_2{\cdot}H + IBr \quad (\text{type } B_1)$$

EXPERIMENTAL.

Side-chain Bromination of Nitro-p-*xylene*.—Dry bromine (30 g.) was very gradually added to a solution of nitro-*p*-xylene (25·0 g.)

in glacial acetic acid (30 c.c.) under reflux in a glycerol bath at 120°, the crystalline deposit which collected in the condenser being returned from time to time to the reaction mixture. The deep red product was poured into water, neutralised with sodium carbonate, and extracted with ether, a process which removed a small amount of a tarry substance insoluble both in ether and in water. The residue (28·2 g.) from the ethereal extract, which preliminary experiments had shown to contain unbrominated nitro-*p*-xylene as well as its bromination products, was heated with an excess of 33% alcoholic trimethylamine for 12 hours at 100°, and the quaternary bromides derived from side-chain-brominated products were precipitated by the addition of much dry ether and collected. From the ethereal solution nitro-*p*-xylene (16·3 g.) was recovered by distillation. The bromide precipitate was taken up in boiling alcohol (which removed a very small amount of an insoluble salt which has not yet been investigated), and the quaternary bromide (yield 62%, taking count of the nitro-*p*-xylene recovered), obtained by evaporation of the alcohol, was converted into the corresponding picrate, m. p. 138°, the identification of which is described below. The yield (*vide infra*) corresponds to the formation of not less than 77% of 3-nitro-*p*-xylyl bromide.

*3-Nitro-*p*-xylyl Bromide* [ω(1)-*Bromo-3-nitro-*p*-xylene*].—The bromination product obtained from the ethereal extract (above) is largely solid and a proportion of it (37%, based on the nitro-*p*-xylene used, *less* that recovered) was isolated in the pure condition. *3-Nitro-*p*-xylyl bromide* crystallises from methyl alcohol in needles, m. p. 76° (Found: C, 42·4; H, 3·6. $C_8H_8O_2NBr$ requires C, 41·8; H, 3·5%). On treatment with alcoholic trimethylamine under the conditions mentioned in the preceding paragraph it is converted into the same quaternary bromide in 81% yield. The mother-liquors from the crystalline bromonitro-hydrocarbon contained a further quantity of this substance, together with unchanged nitro-*p*-xylene, and the mixture was therefore treated with trimethylamine; a yield of the quaternary salt stoicheiometrically equivalent to a further 31% of 3-nitro-*p*-xylyl bromide was then obtained. The total quantity of this compound produced cannot therefore be less than 68%, and, since the quaternary salt is produced in 81% yield from the pure bromide, is probably not less than 76%, which agrees with the previous figure. Since part of the remainder represents unidentified material, this figure is a minimum for the proportion of substitution in the *m*-methyl group.

*3-Nitro-*p*-xylyl-ω-trimethylammonium Picrate.*—3-Nitro-*p*-xylyl chloride was prepared by the action of dichlorodimethyl ether on *o*-nitrotoluene (Stephen, Short, and Gladding, J., 1920, **117**, 524),

and had m. p. 48° (not 45° as recorded, *loc. cit.*). Treatment with alcoholic trimethylamine yielded a quaternary ammonium *chloride*, which was precipitated by addition of dry ether. The corresponding *picrate* separated from dilute alcohol in needles, m. p. 138° (Found : C, 47·2; H, 4·6. $C_{17}H_{19}O_9N_5$ requires C, 46·7; H, 4·3%), and was identical with the same salt obtained, as described above, from the bromination product of nitro-*p*-xylene. This identification orients the nitro-*p*-xylyl bromide, m. p. 76°.

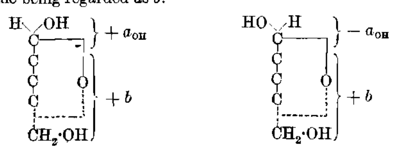
We wish to thank the Chemical Society for a grant which has defrayed much of the cost of this work.

THE UNIVERSITY, LEEDS. [*Received, March 22nd, 1928.*]

CLVII.—*Ring Structure and Optical Relationships in the Mannose–Rhamnose–Lyxose Series of Sugars. Isolation of a New Form of Lyxose.*

By WALTER NORMAN HAWORTH and EDMUND LANGLEY HIRST.

C. S. HUDSON'S application to the sugar group of the "principle of optical superposition" suggested by van 't Hoff has been of great service in the study of the complex problems of optical isomerism in the series glucose–galactose–arabinose–xylose. The calculations of molecular-rotation values based on the consideration of two parts of the sugar molecule have led to strikingly concordant results in that series for the estimation of the rotational effect of the groups attached to the reducing carbon atom 1. In an aldose, these groups, a_{OH} and $-a_{OH}$, correspond to the spatial distribution in the α- nd β-isomerides of any one sugar, the remaining portion of the iolecule being regarded as *b*.

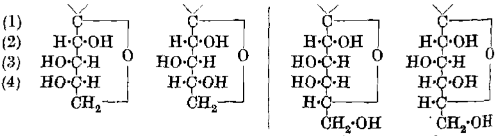
(1) 

ı the methylglucosides, the *a* value becomes $\pm a_{OMe}$ and in the omeric acetates $\pm a_{OAc}$, etc. The molecular-rotational increment ın be obtained by difference: $(+a_{OH} + b) - (-a_{OH} + b)$, and ıch differences approximate very closely in the glucose–galactose–rabinose–xylose series to the constant values $a_{OH} = 8{,}500$; $a_{OMe} =$ 8,500; $a_{OAc} = 19{,}100$, and so on for other types of groupings,

Using these values in those cases where one stereochemical form is unknown, Hudson has been successful in calculating the rotation of the missing form, and in several cases the values so derived have been verified by the subsequent discovery of the new form.

Similarly the magnitude $2b$ can be calculated by addition of the molecular rotations of two α- and β-forms, thus: $(+a_{OH} + b) + (-a_{OH} + b)$. Here the considerations are more complex, and any departures from the regularity of the additive principle are more likely to become manifest. An example is that of the $b_{arabinose}$ value. According as this is calculated from the observed molecular rotation of (1) the sugar or (2) the methylarabinoside, $b_{arabinose} = 18{,}700$ or 21,800. A difference of 3,100 (increased to over 4,000 by taking alternative standards) may not be considered serious when the total rotation is large, but the percentage error is likely to be very marked when the total rotation is small. This percentage error is liable to be much exaggerated when the rotational values are dissected to give the individual contributions of the several carbon atoms in the b portion.

A recent attempt has been made by Hudson (*J. Amer. Chem. Soc.*, 1926, **48**, 1424, 1434) to correlate the values for an intermediate grouping in the sugar chain. Thus methylarahinoside (I) and methylxyloside (II) differ only in the orientation of the groups at the fourth carbon atom. Similarly also methylgalactoside (III) and methylglucoside (IV) differ only at C_4 if the ring structure of each be considered identical.



(I.) (II.) (III.) (IV.)

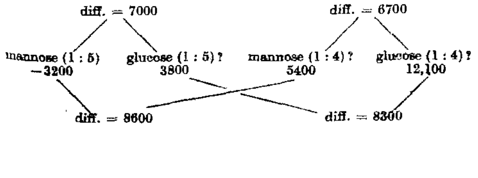
On the basis of the additive principle of optical superpositior Hudson assigns a constant value in each sugar derivative to (which is + or − according as the OH at this carbon atom is directe to the left or to the right. If the rest of the molecule other than (be called p for the pentosides and h for the hexosides, both thes factors are eliminated by subtraction. Thus for (I) and (II) w have $+C_4 + p = 40{,}300$ and $-C_4 + p = 25{,}200$, which giv $C_4 = 7{,}550$. Also for (III) and (IV) we have $+C_4 + h$ and $-C_4 +$ On the chemical evidence of determinations of structure Hudsc accepts the six-atom ring for arabinoside (I), xyloside (II), a galactoside (III). He uses the present calculations, however,

test the ring structure of the known α-methylglucoside. Now for (III) $+C_4 + h = 37{,}380$, and from these data the magnitude of (IV), $+C_4 + h = x$, can be ascertained by adopting the above value for C_4, and it is thus found that $x = 22{,}280$. This falls short of the observed molecular rotation of α-methylglucoside (30,630) by 8,350, and corresponds to a specific rotation of +115° for the latter instead of the observed $[\alpha]_D = +158°$.

On these grounds Hudson rejects the six-atom ring structure for α-methylglucoside, which he considers has a five-atom ring. Such a conclusion is at variance with other and direct chemical evidence which we have contributed (Charlton, Haworth, and Peat, J., 1926, 89; Hirst, *ibid.*, p. 350; Haworth, Hirst, and Miller, J., 1927, 2436). Moreover this latter evidence is as convincing as that which Hudson had already accepted for the pentosides and hexoside, (I), (II), and (III), as the basis of these calculations.

The clear inference to be drawn is that C_4 in the pentoside series has a different value from C_4 in the hexoside series. We hold that even on the principle of optical superposition this could only be expected (compare Drew and Haworth, J., 1926, 2303). Hudson prefers, however, the contrary view.

Now it appears that the hypothetical value of $[M]_D$ (22,280) = x, ached by Hudson, corresponds to a magnitude for $b_{glucose}$ of 3,780, which differs from the observed value of +12,100 by 8,320. This happens also to be about the numerical difference ,600) between $b_{mannose\ (\alpha\text{-})} = -3{,}200$ (calculated from α-mannose) ıd $b_{mannose\ (\beta\text{-})} = +5{,}400$ (calculated from β-mannose). Hudson ere makes the assumption that the agreement between these umerical differences is ascribable to one and the same cause, amely, the differences contributed by a 1 : 5- and a 1 : 4-oxide ring, ıd assigns, therefore, the six-atom ring (1 : 5) structure to α-mannose on these grounds, and the five-atom ring (1 : 4) structure to ·mannose. He is led to suggest that there should exist not only n α-mannose (1 : 4) and a β-mannose (1 : 5) which are at present nknown, but also two new forms of methylglucoside (1 : 5), α- and ·, as well as two new forms of glucose corresponding to these. The umerical features of the following system would then, approximtely, be made to balance :



On the assumption of the possibility of the existence of these unknown sugar forms, the following table of "epimeric differences" can be constructed:

1 : 4	α-methylglucoside (known), $[\alpha]_D$	+158°	diff. = 33°.
	α-methylmannoside (unknown)	+125°	
1 : 5	α-methylglucoside (unknown)	+115°	diff. = 36°.
	α-methylmannoside (known)	+ 79°	
1 : 4	α-methylglucoside tetra-acetate (known)	+130°	diff. = 28°.
	α-methylmannoside tetra-acetate (unknown)	+102°	
1 : 5	α-methylglucoside tetra-acetate (unknown)	+83°	diff. = 34°.
	α-methylmannoside tetra-acetate (known)	+49°	

These hypothetical "epimeric differences" are now made the basis, in Hudson's paper, of a calculation of the expected specific rotations of ten compounds related to α- and β-methylglucosides regarded as 1 : 4 (butylene) oxides.

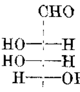
A table of agreement with the observed values for these compounds is then given. The scheme of correlation is dependent upon the fortuitous agreement between the value of $b_{glucose}$ calculated by the above methods and that value of the coefficient (3,500) which is required to make $b_{mannose\ (1:4)}$ minus $b_{mannose\ (1:5)}$ equal to $b_{glucose\ (1:4)}$ minus $b_{glucose\ (1:5)}$. It will necessarily follow then that the "epimeric differences" $b_{mannose\ (1:5)}$ minus $b_{glucose\ (1:5)}$ and $b_{mannose\ (1:4)}$ minus $b_{glucose\ (1:4)}$ are also equal to one another.

This is the relationship which lies behind the impressive agreement of the observed and calculated rotations of glucose derivatives given by Hudson in support of his contention that α-methylglucoside is a 1 : 4 oxide. *The only inference that can be drawn from his tabl is that the rotational value of* C_2, *calculated from appropriately selecte standards, is approximately constant.* Support for this view may b found in the rotations of known substances, without introducin any assumptions either of ring structure or of the existence o hypothetical compounds. For example, the real or observe epimeric differences between several of the α-mannose and α-glucos derivatives and between several of the β-mannose and β-glucos derivatives are regular. This particular statistical method o reaching a conclusion on ring structure may therefore be set aside.

Let us consider the optical relationships in the mannose–rhamnose lyxose series from another point of view. Calculations of th coefficients expressed as a_{OH}, a_{OMe}, $b_{mannose}$, $b_{rhamnose}$, b_{lyxose} base solely on the known rotations of compounds in this serie *without reference to glucose and galactose*, have revealed the interestin fact that the rotations of the different forms of the three sugars an of their glucosides may be accommodated with consistency withi a single scheme similar to that worked out by Hudson for tl glucose–galactose series. Had these sugars initially been mo

readily available, the possibility would have arisen of their being accepted as standards, and an anomalous behaviour would then have been attributed to the present "standard" series comprising glucose and galactose. It seems, therefore, that the hypothesis of different ring structures in α- and β-mannoses affords little or no assistance in interpreting the experimental observations. In the absence of definite chemical evidence to the contrary we consider it would be most helpful to the future study of the problem to regard α- and β-mannose as being not necessarily dissimilar in ring structure, and to seek the reason for divergences in optical and other physical properties occasioned by the special arrangement of hydroxyl groups in mannose and the related sugars rhamnose and lyxose.

It will be apparent from the foregoing account that further observations on the rotational behaviour of these systems containing the grouping (V) would be of interest. For these reasons we have commenced a detailed study of lyxose and its derivatives, which has resulted in the first place in the discovery of a new crystalline form of lyxose differing markedly from that previously described.


(V.)

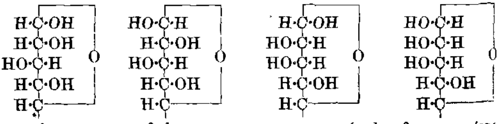
At the outset no crystalline lyxose was available, and a specimen was prepared by Weerman's method (*Rec. trav. chim.*, 1917, **37**, 16). This material was recrystallised from alcohol, and the pure lyxose obtained was not the α-variety described by other workers. For this α-form Hudson and Yanowsky (*J. Amer. Chem. Soc.*, 1917, **39**, 1034) found $[\alpha]_D$ +5·5° in water, decreasing to a constant value −14°, and Weerman, who appears to have obtained the same substance, gives m. p. 106—107°. The new variety showed, however, a higher m. p., 117—118°, and was strongly lævorotatory, giving in aqueous solution $[\alpha]_D$ −70°, decreasing in less than 30 minutes to the same constant value as the α-form, −14°. The inter-relationship between the new form and the other form of lyxose was established by the following observations: (1) the equilibrium value of the specific rotation was $[\alpha]_D$ −14°; (2) the *p*-bromophenylhydrazone, m. p. 155—157°, and the osazone, m. p. 157—160°, were identical with the corresponding derivatives prepared from α-lyxose; (3) the new variety was converted in good yield into crystalline α-methyl-lyxoside, m. p. 108°, $[\alpha]_D$ +59°, which has been described by Phelps and Hudson (*J. Amer. Chem. Soc.*, 1926, **48**, 503).

The molecular-rotation difference between α-lyxose and the new variety is 11,000, comparable with 8,500 and 10,000, respectively, for mannose and rhamnose. The analogy with mannose was further extended by measuring the velocity coefficient for the mutarotation

of the new form of lyxose: the course of the change followed the unimolecular law and the velocity coefficient was approximately equal in value to that found by Hudson and Yanowsky for α-lyxose. Riiber and Minsaas (*Ber.*, 1927, **60**, 2402) have observed similar regularities in the mutarotation of α- and β-mannose.

The simplest and most obvious interpretation of these results is to regard the new substance as the β-form of lyxose, corresponding to the α-form in the same way as does β-mannose to α-mannose, inasmuch as similar and anomalous optical behaviour is shown by lyxose, mannose and rhamnose. This is the explanation favoured by the present authors. The situation is complicated, however, by the fact that the specific rotation of the hitherto unknown β-lyxose has been calculated by Hudson and Yanowsky (*loc. cit.*), whose estimated value, obtained by their solubility method, is $[\alpha]_D$ −36° instead of our observed value −70°. The discrepancy may be viewed from another angle by considering the proportion in which α- and β-lyxose are considered by Hudson to be present in the equilibrium mixture in 90% alcohol. This is given as 68% α- to 32% β- and it is significant that the proportion of α- is markedly less than is the case for either mannose or rhamnose. There appeared to be no particular reason for such a divergence and we therefore decided to repeat the solubility experiments, using the properties of the new β-form to calculate the rotation of the α-form. We obtained for α-lyxose the calculated value of $[\alpha]_D$ +5°, which is very close to the observed value +5·5°. This corresponds to an equilibrium mixture (in 90% alcohol) containing 83% of the α-form.

When the α- and β-forms of a sugar are considered from the point of view of the *cis*- and *trans*-relationships of the hydroxyl groups on the first and second carbon atoms, a striking regularity is manifested. This may be expressed by the statement that in the equilibrium mixture of the two isomerides the tendency is for the *trans*-form to predominate.



α-glucose (*cis*) — β-glucose (*trans*) — α-mannose (and rhamnose and lyxose) (*trans*) — β-mannose (and rhamnose and lyxose) (*cis*)

When there are two *cis*-hydroxyl groups as in mannose, rhamnose and lyxose, the preponderance of the *trans*-form at equilibrium tends to be greater in alcohol than in water, whereas the reverse is

the case when the hydroxyl groups on carbon atoms 2 and 3 are *trans* to one another. Detailed figures are given in the accompanying table,* where column (B) shows the percentage of one form in the equilibrium mixture, as obtained by direct measurement in Hudson and Yanowsky's solubility experiments. The figures for lyxose are, however, those obtained during the present investigation. In column (A) is given the percentage of the *trans*-isomeride in the equilibrium mixture in aqueous solution, the figure being calculated from the known rotation values for the pure forms on the assumption that the equilibrium mixture contains only the α- and β-forms of the sugar. (The evidence at present available shows that there is little reason for doubting the essential trnth of this assumption.) In addition, the fact that α-glucose and α-mannose are respectively *cis*- and *trans*-compounds in this sense may perhaps serve to explain the various small differences in certain physical properties noted by Riiber and Minsaas (*loc. cit.*) when comparing glucose and mannose.

Sugar.	*trans*-Variety.	(A) Proportion of *trans*-form at equilibrium in water (%).	(B) Proportion of *cis*-form present in aqueous alcohol (%).
Glucose	β-	66	44·7 α-
Galactose	β-	69	41·8 α
Xylose	β-	65	44 α-
Arabinose	α-	58	38 β-
Lyxose	α-	75	17 β-
Mannose	α-	62	18 β-
Rhamnose	α-	73	15 β-
α-Glucoheptose	β-	89	12 α-

Since the proportion of the α- and β-forms at equilibrium is intimately connected with the relative solubilities of the two varieties, it is apparent from the above table that there is a relationship between the *cis*- and *trans*-nature of the hydroxyl groups and the relative solubilities of the α- and β-forms. This is most pronounced in those cases which afford a possibility for one isomeride to have three adjacent *cis*-hydroxyl groups (mannose, lyxose, rhamnose), and an accumulation of two or three such groupings gives precisely the conditions appropriate for the formation of co-ordinate linkages. The question whether such linkages are formed is obviously a matter for further inquiry. We are endeavouring to test this idea as a possible means of explaining both the solubility relationships amongst the α- and β-forms of sugar derivatives and the optical anomalies displayed in the mannose series when compared with the glucose–galactose series.

* A similar table can be constructed for the disaccharides melibiose, maltose, lactose, and cellobiose, where in every case the *trans*-form is present in excess at equilibrium.

Experimental.

Preparation of Lyxose.—A pure specimen of lyxose was obtained from crystalline galactonolactone by following, with slight modifications, the directions of Weerman (*loc. cit.*). Under the conditions described, difficulty was experienced in separating the lyxose, in the form of its insoluble *p*-bromophenylhydrazone, from the accompanying mineral salts. In order to carry out this operation successfully the lyxose solution must be concentrated and the *p*-bromophenylhydrazine must be dissolved in the minimum quantity of alcohol. If necessary, the solution containing lyxose *p*-bromophenylhydrazone is evaporated to dryness and the mineral salts are removed by solution in water. Lyxose *p*-bromophenylhydrazone is most easily purified by recrystallisation from hot water.

The lyxose regenerated from the *p*-bromophenylhydrazone was in the form of a syrup. This was exposed to the air from time to time and rubbed with a glass rod, until at the end of 14 days rapid crystallisation commenced. Recrystallisation from alcohol gave needles, m. p. 117—118°, which were slightly hygroscopic (compare Ruff and Ollendorf, *Ber.*, 1900, **33**, 1798).

After several preliminary experiments by Weerman's and by Ruff and Ollendorf's method the following procedure was found to be the most convenient for the preparation of larger quantities of lyxose. Calcium galactonate (Clowes and Tollens, *Annalen*, 1900, **310**, 166), which did not require to be separated completely from calcium bromide, was treated with hydrogen peroxide and ferric acetate according to the method of Ruff and Ollendorf (*loc. cit.*). After removal of the greater portion of the calcium salts in the way described by these authors, the pentose content of an aliquot portion of the resulting alcoholic solution of lyxose was estimated by the furfural method. The remainder of the alcoholic solution was then concentrated to small bulk and the calculated quantity of *p*-bromophenylhydrazine, dissolved in the minimum quantity of alcohol, was added. Lyxose *p*-bromophenylhydrazone soon crystallised and a further amount was obtained by addition of water to the mother-liquor. Recrystallisation from water gave a pure product from which lyxose was regenerated by treatment with benzaldehyde in the usual manner. The syrupy lyxose was finally dissolved in 3—4 volumes of absolute alcohol and on addition of a nucleus rapid crystallisation ensued. The yield of crystalline lyxose from the *p*-bromophenylhydrazone averaged 80—90% of the theoretical. The overall yield from galactose was low (10%), owing mainly to the small proportion of calcium galactonate which is degraded, even under the most favourable conditions.

The crude β-lyxose thus obtained had m. p. 114—115° and re-

crystallisation from alcohol yielded the pure product in needles, m. p. 117—118°. These were very soluble in water but only slightly soluble in absolute alcohol. Measurements in 90% and 85% alcohol (by weight) at 18° gave respectively solubilities of 0·8 and 1·7 g. per 100 c.c. The new compound was strongly lævorotatory in aqueous solution and showed rapid mutarotation to a final equilibrium value $[\alpha]_D$ −14°. The mutarotation followed a unimolecular course, the constant $k_1 + k_2$ being 0·082 at 21° and 0·056 at 17°. The initial value of $[\alpha]_D$ in water was calculated to be −70°, and the observed values in 90% ethyl alcohol were $[\alpha]_{5461}$ −80° (initial value) and −9° (equilibrium value). Detailed figures for the mutarotation are given in the following tables, the value of $k_1 + k_2$ being calculated from the formula $k_1 + k_2 = 1/t \cdot \log\{(r_0 - r_\infty)/(r - r_\infty)\}$. The first column gives in minutes the time elapsed after solution of the lyxose. The dissolution in water was complete in 15 seconds. 'or α-lyxose Hudson and Yanowsky found $k_1 + k_2 = 0{\cdot}065$ at 20°.

Solvent—water. Temp. 21°. $c = 3{\cdot}83$.

Time (mins.).	$[\alpha]_D$.	$k_1 + k_2$.
1	−60°	—
2	52·5	0·078
4	40	0·083
6	32·5	0·079
8	26·5	0·081
10	22	0·084
12	19·5	0·084
14	17	0·091
18	15	—
∞	14	—

For $t = 0$, $[\alpha]_D = -70°$ by calculation.

Solvent—water. Temp. 17°. $c = 1{\cdot}1$.

Time (mins.).	$[\alpha]_D$.	$k_1 + k_2$.
4	−48°	—
7	37	0·057
12	27	0·052
14	23·5	0·055
16	21	0·057
18	19	0·059
20	18	0·058
22	17	0·059
∞	14	—

For $t = 0$, $[\alpha]_D = -71°$ by calculation.

The β-lyxose remained unchanged after prolonged contact with '0% alcohol and up to the present we have been unable to induce he α-form to separate from solution.

Calculation of the Rotation of α-Lyxose by the Method of Hudson 'nd Yanowsky.—Crystalline β-lyxose (m. p. 117—118°) was finely owdered and shaken for 6 minutes with 90% ethyl alcohol. After iltration the solution was allowed to reach equilibrium; the reading $_{5461}$ −0·07° was then recorded, corresponding to a concentration f 0·8 g. per 100 c.c. Another sample was shaken for several hours ith 90% alcohol; after filtration, the reading α_{5461} −0·43° was btained, or $c = 4{\cdot}8$. The equilibrium mixture therefore conained 0·8 g. of β-lyxose and 4·0 g. of α-lyxose per 100 c.c. Since in '0% alcohol $[\alpha]_{5461}$ for β-lyxose was found to be −80°, and the quilibrium value −9°, the calculated value of $[\alpha]_{5461}$ for the ·-lyxose was found to be +5°. A repetition of the experiment with

85% alcohol gave 1·7 as the initial solubility of β-lyxose in this solvent, and as the final solubility of the equilibrium mixture was 10·5, the calculated value was $[\alpha]_{5461}$ +5° for α-lyxose. The observed value corresponding to $[\alpha]_D$ +5·5° was $[\alpha]_{5461}$ 6·5°.

Conversion of β-Lyxose into Known Derivatives.—The *p*-bromophenylhydrazone (needles, m. p. 155—157°) and the characteristic osazone, identical with xylosazone, m. p. 157—160°, were prepared and found to be identical with the known compounds. A further proof of identity was obtained by the preparation of α-methyl-lyxoside from β-lyxose. A solution of the sugar in methyl alcohol containing 1% of hydrogen chloride was boiled for 2 hours as described by Phelps and Hudson (*loc. cit.*). The acid was neutralised with lead carbonate and the resulting colourless solution was evaporated to a syrup, which soon crystallised. The solubility of α-methyl-lyxoside in ethyl acetate was found to be so great as to render the method of recrystallisation recommended by Phelps and Hudson difficult to carry out satisfactorily with small quantities of material. The following method works well with quantities of a centigram upwards. The substance was dissolved in a very little absolute ethyl alcohol, and petroleum (b. p. 60—80°; light petroleum b. p. 40—60°, is useless) was added carefully until a faint permanent cloudiness appeared. This was removed by addition of a drop of alcohol and thereafter α-methyl-lyxoside crystallised rapidly. Two crystallisations were sufficient to give the pure substance, m. p. 108—109°, $[\alpha]_D$ +59° in water (c = 1). Yield, 70%.

The authors wish to thank the Chemical Society for the award of a grant which has partly defrayed the cost of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, February 17th, 1928.*]

CLVIII.—*Equilibrium in Solutions. A Note on "The Activity Theory of Reaction Velocity."*

By W. F. KENRICK WYNNE-JONES.

IN a recent paper (J., 1927, 2761), Soper and Pryde, in discussing the velocity of reaction in solution, have considered the equilibrium in a system containing, for example, hydrogen chloride and its ions $HCl \rightleftharpoons H^{\cdot} + Cl'$, for which process they advance as the criterion of equilibrium

$$-dF_{HCl} + dF_{H^{\cdot}} + dF_{Cl'} + dF_{medium} = 0 \quad . \quad . \quad . \quad (1)$$

where the dF's refer to changes in the partial free energies of the various species.

On the basis of this equation Soper, both in the paper mentioned and elsewhere (*J. Physical Chem.*, 1927, **31**, 1790; 1928, **32**, 67), has discussed in detail the thermodynamic properties of electrolytic solutions. The chief results of this discussion are the derivation of a new activity relationship for ions involved in equilibria with neutral molecules, and the deduction of a modified equation for the velocity of ionic reactions.

So far as the activity relations are concerned, Soper asserts that wherever one is considering the transfer of ions from one concentration to another the activities of these ions are related to their partial free energies; if, however, an equilibrium be considered, the activities are determined by the total free energy of the solution. Applying these conceptions, he has derived, on the basis of the Debye–Hückel theory, the two following equations connecting the activity coefficient with the ionic strength for aqueous solutions at 25°: $\log f = -0{\cdot}505z^2\sqrt{\mu}$, where the partial free energies are concerned, and $\log f = -0{\cdot}33z^2\sqrt{\mu}$, where the total free energy enters.

In the velocity of ionic reactions, Soper considers the second equation to determine the activity coefficients of the ions and consequently deduces for a bimolecular reaction between ions

$$v = kc_Ac_Bf_Af_B/f_{AB}$$

where

$$f_Af_B/f_{AB} = 0{\cdot}66z_Az_B\sqrt{\mu}.$$

This equation is the form to which the general reaction velocity equation of Brønsted reduces for the special case of an ionic reaction. In Brønsted's equation, however, the kinetic activity factor is given by

$$f_Af_B/f_{AB} = 1{\cdot}00z_Az_B\sqrt{\mu}.$$

It is evident that, if Soper's contentions are valid, he has derived relationships of great significance, and has, in fact, revolutionised the thermodynamic treatment of electrolytic solutions. Consequently, it is of importance to examine his fundamental postulates and to see how far they are in accord with thermodynamics.

In the first place, it must be pointed out that it is not very logical to restrict the application of a thermodynamic equation, such as (1), to ions, and to employ another equation for neutral molecules. Soper attempts to justify this by the argument that the magnitude of the term $dF_{med.}$ is greater for ions than for neutral molecules; but such a difference in magnitude is not a difference in principle such as to justify the employment of two different equilibrium equations. Further, the assignment of two values to a potential

function under the same conditions seems in serious conflict with thermodynamics.

Leaving aside such general considerations, let us take a reaction such as A + B + . . . $\rightleftharpoons$ P + Q + ... The free energy of such a system will, at constant temperature and pressure, be a function of the number of molecules of each species present; hence $dF = (\partial F/\partial n_A)dn_A + (\partial F/\partial n_B)dn_B + \ldots + (\partial F/\partial n_{med.})dn_{med.}$, where $n_A, n_B, \ldots n_{med.}$ refer to A, B, etc., and the medium. Employing G. N. Lewis's notation $\bar{F} = (\partial F/\partial n)$ for the partial molar free energy of any species, we have

$$dF = \bar{F}_A \,.\, dn_A + \bar{F}_B \,.\, dn_B + \ldots + \bar{F}_{med.} \,.\, dn_{med.}.$$

Since at equilibrium a small displacement is unattended by a change in the free energy of the system, $dF = 0$, *i.e.*,

$$0 = \bar{F}_A \,.\, dn_A + \bar{F}_B \,.\, dn_B + \ldots \bar{F}_{med.} \,.\, dn_{med.} \quad . \quad (2)$$

On comparing (2) with (1), it is noticeable that (1) contains no terms for the change in the number of molecules, and this omission is the crucial error for the further development of the equilibrium criterion; for when we are considering a reaction in solution, the solvent does not occur on one side only of the reaction scheme, and consequently a small displacement of the equilibrium does not involve any change in the number of solvent molecules; therefore the equilibrium condition is

$$0 = \bar{F}_A \,.\, dn_A + \bar{F}_B \,.\, dn_B + \ldots + 0 \,.\, \bar{F}_{med.}.$$

Thus, by reproducing the thermodynamic derivation, we are able to see that the classical expression which omits the term for the free energy of the solvent is completely valid even for ionic equilibria.

However, in order to make the matter still clearer and more tangible, we may examine the method employed by Soper in the deduction of his formula for reaction velocity. He states: "The total free electrical energy of a solution of n ions found by charging them reversibly is $\frac{1}{2}nz\epsilon\psi$, where ψ is the potential at one of these ions due to the surrounding 'ion-atmosphere.' Part of this electrical free energy resides in the medium, but change in the partial free electrical energy of the ions is attended simultaneously by a change in the electrical free energy of the medium. The total potential energy possessed by an ion in virtue of its charge is thus $\frac{1}{2}z\epsilon\psi$ . . . ."

Soper is fully aware that the term $\frac{1}{2}nz\epsilon\psi$ is the total electrical free energy of the solution, but he seems to think that the potential energy of an ion within this solution may be obtained by dividing this term by the number of ions. The true value of the potential energy of a single ion is, however, the work obtained by discharging

the ion reversibly; this is given by $W = \int_0^\epsilon z\psi dz = \frac{1}{2}z\epsilon\psi$ as shown by Güntelberg. If now we substitute this term wherever Soper uses $\frac{1}{3}z\epsilon\psi$, the spurious factor 2/3 disappears and the ordinary activity relations, as well as the original form of Brønsted's velocity equation, are obtained. It must therefore be concluded that the various modifications proposed are all alike without foundation in thermodynamics.

So far as the particular question of reaction velocity in solution is concerned, the agreement with experiment obtained by Soper for his expression is a consequence of the operation of the linear terms in the Debye-Hückel equation for activity coefficients, *viz.*, $-\log f = Ac^{\frac{1}{2}} + Bc$. The introduction of these terms will, in the range 0·04—1·0*N*, lower the kinetic activity factor to approximately two-thirds of its limiting value.

In conclusion, it may be stated that the Brønsted formula has proved entirely satisfactory wherever it is applied within the region for which it was originally developed. When it is remembered that the formula is successful in predicting salt effects of the most varied type and magnitude, for which previous theories have been entirely unable to account, it will be realised that the formula represents a very marked step in advance, and may, so far as the region of dilute solutions is concerned, be considered a solution of the problem.

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COPENHAGEN. [*Received, February 6th*, 1928.]

CLIX.—*Equilibrium in Electrolyte Solutions and the Reaction-velocity Equation.*

By FREDERICK GEORGE SOPER.

OBJECTIONS have been raised (Wynne-Jones, preceding paper) to the interpretation of the results obtained for the rate of interaction of hydrochloric acid and a chloroamine (J., 1927, 2761) on two grounds—(*a*) the condition of equilibrium in an electrolytic solution, and (*b*) the nature of the reaction-velocity equation.

The condition of equilibrium in a system containing hydrogen chloride and its ions was given (*loc. cit.*, p. 2766) as

$$-dF_{HCl} + dF_{H^{\cdot}} + dF_{Cl'} + dF_{medium} = 0$$

where the dF's refer to the changes in the partial free energies of the various species and dF_{medium} has a finite value.* Wynne-

* An erroneous value for dF_{medium} was employed in *J. Physical Chem.*, 1928, **32**, 67, and the conclusions there reached are withdrawn.

Jones asserts that, since the number of solvent molecules is unchanged by the slight displacement,

$$dF_{medium}\ (i.e.,\ \partial F/\partial n_{medium}\ .\ dn_{medium}) = 0.$$

The point of view is dependent on one's conception of an ion. It is legitimate to regard the ion as an unhydrated particle and to evaluate its partial free energy on this assumption. It would also be legitimate to evaluate the partial free energy of, say, sodium in water by *additions of metallic sodium to an aqueous sodium hydroxide* solution, but this partial free energy would not be equal, or even proportional, to that of the sodium hydroxide which is actually present. From the reaction-velocity standpoint, it is obviously desirable to deal as far as possible with the ions actually existing, *i.e.*, with the hydrated complexes. On this view, a slight displacement of the equilibrium $HCl \longrightarrow H^{\cdot} + Cl'$ involves a change in the number of free solvent molecules and in the free energy of the medium, a fact which should be allowed for in the condition for *equilibrium. The activity of hydrogen chloride measured electro*metrically is therefore only proportional to the activity of the ions if they are unhydrated. It is, however, proportional to the activity of the un-ionised hydrogen chloride, as was stated.

The same conclusions may be reached more directly by writing the ionic equilibrium as follows:

$$HCl + (x + y)\ H_2O \rightleftharpoons H^{\cdot},xH_2O + Cl',yH_2O$$

which necessitates that

$$a_{H^{\cdot}xH_2O}\ a_{Cl'yH_2O}/a_{HCl}\ a_{H_2O}^{x+y} = K$$

i.e., the activities of the ions involve the variable activity of the solvent.

The evaluation of the free energy change of the medium (*J. Physical Chem.*, 1928, **32**, 67) as $nz^2\epsilon^2\kappa/6D$ is incorrect. It should be amended to $z^2\epsilon^2\kappa n_1 dn_0/n_0$, where dn_0 is the number of solvent molecules bound by dn_1 ions, and n_1 and n_0 are the number of ions and solvent molecules per c.c. This term cannot at present be evaluated, and, if it is neglected, the free electrical energy of an ion to be used in determining the critical increment of an ionic reaction is $-z^2\epsilon^2\kappa/2D$ (*J. Physical Chem.*, 1927, **31**, 1790). The reaction velocity equation for ions then reduces to

$$\log k = C + 1{\cdot}00 z_A z_B \sqrt{\mu}$$

which is the form used by Brønsted (Brønsted and Livingston, *J. Amer. Chem. Soc.*, 1927, **49**, 435).

It may be noted, however, that the assumptions underlying t

derivation of this equation in the two cases are different. That derived by the author assumes that the energy of activation is sensibly constant in aqueous solution and is made up of energy given by a Maxwell distribution and of potential energy possessed by the reacting ions due to their charges. In the Brønsted equation the activity coefficient of the critical complex, f_x (which is also a measure of the critical increment; Brønsted, *Z. physikal. Chem.*, 1925, **115**, 343), is assumed to vary with the ionic strength as would any other ion of the same valency. A differentiation between the equations would appear to be possible here. Secondly, the similarity in the form of the equations depends on the reagents being electrically charged.

The rate of interaction of hydrogen chloride and a chloroamine was found to be directly proportional to the activities of the reagents measured in the presence of each other. There was no appearance of deviation indicating the necessity of an f_x term for neutral molecules, although the electrolyte concentration was varied from 0·1 to 1·5 *M*.

UNIVERSITY COLLEGE OF N. WALES,
BANGOR. [*Received, February 27th*, 1928.]

CLX.—*The Conductivity of Copper Hydrosols.*

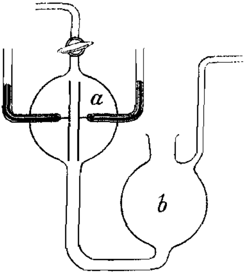
By HUMPHREY DESMOND MURRAY.

MEASUREMENT of the conductivities of metal hydrosols prepared by Bredig's method was undertaken with a view to examine the ionic equilibrium in such sols. It was found, however, that the concentration of stabilising electrolyte was so large as to preclude any evidence being obtained of the equilibrium between ions on the particle surface and those in solution.

Measurements were made in a cell of the form shown in Fig. 1, which was placed in a thermostat at 25°. A measured volume of water of conductivity averaging 0·8 gemmho was placed in the vessel *b*. The conductivity of this water could be kept constant for 7—14 days. At first a screw-adjusted spark gap was fitted in the opening of *b* through a vulcanite stopper, but later two stout metal wires carried by a two-holed rubber bung were found to be more suitable and were boiled with conductivity water on every occasion before use. The top of one of these wires was clamped. By altering the pressure of the clamp, the lower end was made to approach the lower end of the unclamped wire, both being below the surface of the water. By flicking the top of the

unclamped wire, arcing could be started. The copper arc would not run continuously for more than a few seconds and had then to be restruck. The voltage used was 100, and the current passing when the arc had been struck about 5 amps. Electrolyte solutions were run into *b* from a burette, the electrodes being temporarily removed. The side tube of *b* was in communication with the air through soda-lime tubes, and the side tube of *a* was connected through a two-way tap with a water-pump or with the side tube of *b*. In this way the liquid in *b* could be drawn up into *a*, which contained platinum electrodes covered with grey platinum. Its conductivity having been determined, the liquid was allowed to flow back into *b*. This procedure was carried out every 5 minutes during arcing in order to keep the temperature down, and after the addition of electrolyte in order to ensure thorough mixing. Control experiments with conductivity water, but without arcing, showed no increase in conductivity of the water for 12—24 hours.

FIG. 1.

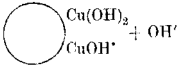


Since these experiments were completed, a paper has been published by Pennycuick (J., 1927, 2600) in which he gives the results of measurements of the conductivity of mixtures of platinum sols and various bases. He finds a slow shift in conductivity on titrating a sol with a base or on altering its temperature. With copper sols this slow alteration in conductivity was not so noticeable provided the cell was thoroughly cleaned out between each experiment. In addition, sols were prepared at 25° (although a greater amount of sputtered metal is produced at this temperature than at 0°) and only small concentrations of electrolytes were added. Copper sols give considerably smaller conductivities than either platinum or silver hydrosols. On continued arcing, the conductivity rises to a value which is constant for the particular sample of water used, thus :

	(1)	(2)
Water alone	$0{\cdot}81 \times 10^{-6}$	$0{\cdot}80 \times 10^{-6}$
Arcing 1 minute	1·48 ,,	1·51 ,,
,, 5 minutes	1·70 ,,	1·73 ,,
,, 10 ,,	1·50 ,,	1·54 ,,
,, 15 ,,	1·48 ,,	1·47 ,,
,, 30 ,,	1·48 ,,	1·46 ,,

After standing for 16 hours both these samples had a conductivity of $1{\cdot}51 \times 10^{-6}$. Beans and Eastlake (*J. Amer. Chem. Soc.*, 1915, 37, 2667) have calculated that the conductivity of the metal particles and their stabilising ions is negligible compared with the above values. It appears probable that the conductivity of copper sols is due to cuprous or cupric hydroxide produced during arcing.

If cupric hydroxide is formed, the charged particle may be represented thus :



Various electrolytes were added to copper sols which had been prepared by arcing for about 10 minutes in 75 c.c. of water. Col. 1

TABLE I.

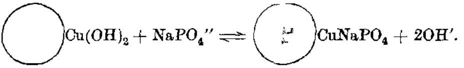
Electrolyte.	1.	2.	3.	4.	5.
NaCl	0	1·6	1·6	—	
	1·25	4·1	4·3	− 0·2	
	2·5	6·5	6·9	− 0·4	
	3·75	9·1	9·3	− 0·2	
	5·0	11·7	11·8	− 0·1	
	7·5	16·5	16·5	±	
	12·5	24·6	24·9	− 0·3	
NaOH	(1) 0	1·5	1·5	—	
	5·0	2·7	3·7	− 1·0	− 0·5
	10·0	5·2	6·4	− 1·2	− 0·6
	15·0	8·1	9·5	− 1·4	− 0·6
	25·0	14·7	16·4	− 1·7	− 0·6
	(2) 5·0	29·2	31·2	− 2·0	− 0·6
	10·0	58·4	60·5	− 2·1	− 0·6
Na_3PO_4	0	1·5	1·5	—	
	0·75	2·5	1·8	+ 0·7	
	1·5	3·6	2·2	+ 1·4	
	2·5	4·4	2·5	+ 1·9	
	5·0	5·3	3·3	+ 2·0	
	7·5	6·4	4·4	+ 2·0	
	12·5	7·3	5·5	+ 1·8	
	17·5	8·3	6·6	+ 1·7	
	22·5	9·2	7·5	+ 1·7	
HNO_3	(1) 0	1·5	1·5	—	
	5·0	2·4	3·8	− 1·4	− 1·1
	10·0	3·2	5·6	− 2·4	− 2·4
	15·0	4·0	7·4	− 3·4	− 3·8
	25·0	5·1	11·3	− 6·2	− 6·5
	(2) 5·0	26·6	85·6	− 59·0	− 58·4
	10·0	52·9	168·9	− 116·0	− 116·2
$AlCl_3$	0	1·6	1·6	—	
	1·25	2·3	2·4	− 0·1	
	2·5	2·9	3·0	− 0·1	
	5·0	4·1	4·4	− 0·3	
	7·5	5·3	5·7	− 0·4	
	25·0	12·1	13·1	− 1·0	

in the table gives the number of c.c. of electrolyte added to 75 c.c. of copper sol; col. 2 the conductivity observed ($\times 10^6$); col. 3 the increase in conductivity observed when the same volume of electrolyte is added to 75 c.c. of conductivity water, plus the conductivity due to the concentration of copper sol in the mixture given in col. 1; col. 4 gives the difference (col. 2—col. 3); and col. 5 gives the value of this difference calculated on the assumptions stated below.

When sodium chloride solution is added to a copper sol, the observed conductivity of the mixture does not differ appreciably from the sum of the calculated conductivities of its components: adsorption of the chloride, if any, is small. With sodium and other hydroxides the conductivity of the mixture is definitely less than that of its components. If this diminution were due to repression of the ionisation of copper hydroxide by sodium hydroxide, the difference calculated on the assumption that the increase in conductivity of the sols over that of the water used is due to cupric and hydroxyl ions only is that given in col. 5. The greater difference observed is probably due to the specific adsorption of sodium hydroxide.

The increase in conductivity when sodium phosphate is added to the sol is more difficult to explain. A similar increase in conductivity is observed when aluminium chloride is added to a negatively charged sol such as platinum. It may possibly be due to the substitution of hydroxyl ious for slower-moving ions by a reaction at the particle surface such as

$$Na_3PO_4 \rightleftharpoons NaPO_4'' + 2Na^{\cdot}$$



When a very dilute acid solution is added to a copper sol, hydrogen and hydroxyl ions are used up and the sol appears to become saturated again with copper hydroxide from the particle surface. Col. 5 gives $C_{HNO_3}(\mu_{H^{\cdot}} - \mu_{Cu^{\cdot\cdot}})$, the difference calculated on this assumption, the repression of ionisation of copper hydroxide by increasing concentration of cupric ions being neglected. The agreement is fairly good and is further evidence for the presence of copper hydroxide in the sol.

Finally, the addition of aluminium chloride shows that this salt probably reacts like an acid with the sol owing to hydrogen ions produced by hydrolysis.

It is to be inferred from these experiments that the particle

surface in copper hydrosols prepared by Bredig's method is largely covered by copper hydroxide, which saturates the water in which the particles are dispersed.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [Received, March 7th, 1928.]

CLXI.—*Acid and Salt Effects in Catalysed Reactions. Part XIII. Inert Salt Effects in the Catalytic Action of Acids.*

By HARRY MEDFORTH DAWSON and ARTHUR KEY.

IT is probable that the velocity of all catalysed reactions will show some alteration when a catalytically inert salt is added to the solution in which the reaction occurs. The effects produced in the case of strong acid catalysts have been frequently examined and various attempts, which need not be recapitulated here, have been made to account for the observed velocity increments. The increased activity of weak acids which results from the addition of catalytically inert salts of the strong acids was established by Arrhenius (*Z. physikal. Chem.*, 1899, **31**, 197), who suggested that this effect was mainly due to an increase in the degree of ionisation of the weak acid. Later writers seem to have associated this with an increase in the dielectric capacity of the reaction medium. The theory of Arrhenius has received some criticism, and an alternative explanation, based in part on the dual theory, has been proposed (compare McBain and Coleman, J., 1914, **105**, 1517; McBain and Kam, J., 1919, **115**, 1332). Since the older arguments for and against the Arrhenius view were based on the classical form of the ionic theory, according to which the strongest acids, as well as salts, are far from completely ionised, they can no longer be considered to have much bearing on the problem as it stands at the present time, when such electrolytes must be regarded as completely ionised or very nearly so.

According to Brönsted (J., 1921, **119**, 574), the modern conception of the strong electrolytes does not invalidate the suggestion made by Arrhenius, and further evidence in support of the view that fully ionised salts increase the ionisation of weak electrolytes has been furnished by observations on the rate of decomposition of diazoacetic ester catalysed by 0·05N-acetic acid in the presence of small quantities of potassium nitrate (Brönsted and Teeter, *J. Physical Chem.*, 1924, **28**, 579). From *E.M.F.* measurements, Harned (*J. Amer. Chem. Soc.*, 1925, **47**, 930) concluded that the

product of the activities of the hydrogen and hydroxyl ions for pure water diminishes at first on the addition of alkali-metal halides, passes through a minimum, and then increases. From this it follows that the ionisation constant of water passes through a maximum value as the concentration of the added salt increases.

The inert salt effects described in this paper have reference, for the most part, to changes in the velocity of the acetone–iodine reaction catalysed by acetic acid in presence of various quantities of the catalytically inert chlorides and nitrates of the alkali metals. Since the results obtained would appear to suggest the existence of some connexion with the conclusions which follow from the application of the concept of thermodynamic activity to the ionisation of weak electrolytes in salt solutions, it seems desirable to recapitulate the standpoint which has been provisionally adopted in the interpretation of our previous catalytic experiments with mixtures of weak acids and their corresponding salts. Such experiments have shown that catalytic activity must be ascribed to weak negative ions and to undissociated molecules, as well as to the hydrogen ion. The identification of the catalytically active constituents would appear to be the first step in the quantitative interpretation of the experimental observations. The further question whether the effects should be expressed in terms of the concentrations of the active entities or in terms of their respective activities has not been ignored, but for the sake of simplicity, and in consideration of the fact that there is no acceptable method for the derivation of individual ion activities, we have interpreted the catalytic data for the above-mentioned mixtures on the assumption (1) that the salts are completely ionised, and (2) that the ionisation of the weak acids is determined by a mass-law constant which is not affected by the salt content of the various solutions. This procedure has been justified by the results and is not to be interpreted in any sense as a denial of the existence of inert salt effects. It is, indeed, probable that such effects are always present, but their importance varies greatly with the particular circumstances. If, for instance, we consider the solution $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H + 1{\cdot}0N\text{-}CH_3{\cdot}CO_2Na$, the concentration of the hydrogen ion is so greatly reduced by the corresponding salt that its catalytic effect in the acetone–iodine reaction can be ignored in comparison with that of the acetate ion and the undissociated acetic acid. If the inert salt effect due to the sodium acetate were such as to produce a change in the hydrogen-ion concentration eqnivalent to an increase of 200% (compare Soper and Pryde, *J.*, 1927, 2761) in the ionisation constant, this would make no difference to the interpretation of our observations on the catalytic activity of this solution. If, indeed, the alteration

were 2000%, the partial velocity due to the hydrogen ion would still be almost negligible.

If, on the other hand, sodium chloride is substituted for sodium acetate, giving a solution $0{\cdot}1N\text{-}CH_3{\cdot}CO_2H + 1{\cdot}0N\text{-}NaCl$, there is now no common ion effect, and since the sodium and chlorine ions are catalytically inert, such solutions obviously afford suitable conditions for the study of the changes which are produced in the catalytic properties of the weak acid by the presence of the inert salt. These changes may be due to an alteration in the ionisation constant of the weak acid, or to variations in the magnitude of the coefficients which express the catalytic activity of the hydrogen ion, the acetate ion, and the undissociated acetic acid.

Although the literature relating to inert salt effects in reactions catalysed by the strong acids is very considerable, and some attention has also been given to the behaviour of weak acids, there appears to have been no systematic investigation of the dependence of these effects on the strength of the catalysing acid. In these circumstances, a comparative study has been made of the changes produced in the velocity of the acetone–iodine reaction by the addition of sodium chloride when the reaction is catalysed by hydrochloric, dichloroacetic, monochloroacetic, or acetic acid in $0{\cdot}1N$-solutions. The results obtained with an acetone concentration of 20 c.c. per litre and from 0·1 to 4·0 molar sodium chloride solutions are shown in Table I, the velocities shown for zero concentration of sodium chloride being those for salt-free solutions. Fig. 1 shows

TABLE I.

Reaction velocities (mols./litre/min.) $\times 10^6$ *at* 25°.

Catalyst.	Concentration of NaCl. 0·0.	0·1.	0·2.	0·5.	1·0.	2·0.	4·0.
$0{\cdot}1N\text{-}CH_3{\cdot}CO_2H$	0·777	—	0·975	1·055	1·143	1·18	1·165
$0{\cdot}1N\text{-}CH_2Cl{\cdot}CO_2H$ ...	7·28	8·06	8·56	9·30	10·1	11·2	12·0
$0{\cdot}1N\text{-}CHCl_2{\cdot}CO_2H$ ...	32·9	34·6	35·8	38·5	42·2	48·6	61·0
$0{\cdot}1N\text{-}HCl$	46·5	—	49·3	53·0	59·5	72·5	111

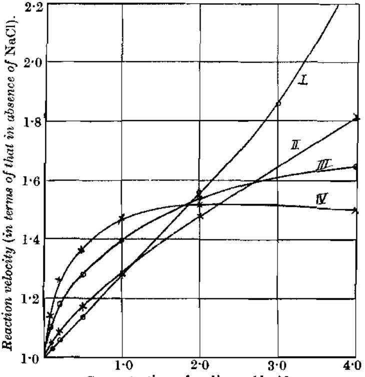
the curves which are obtained when the velocities for the salt solutions, expressed in terms of the corresponding velocity for the pure aqueous solutions, are plotted against the salt concentration.

It is apparent that there is a gradual change in the character of the inert salt effect as the strength of the catalysing acid changes. For hydrochloric acid, the relations are represented by a straight line up to nearly $3N$-sodium chloride; at higher salt concentrations, the velocity increases more rapidly. For the three weaker acids, there is a very marked departure from linearity, and this deviation increases as the strength of the acid diminishes. At low salt con-

centrations, the influence of the inert salt on the reaction velocity is greatest for acetic and least for hydrochloric acid, but the order of the acids is reversed when the relative salt effects at the highest salt concentrations are compared.

With reference to the form of the hydrochloric acid curve, which is similar to that obtained when other acid-catalysed reactions are examined, we would point out that undissociated hydrogen chloride would seem to be the only constituent, other than the hydrogen ion, to which catalytic activity can be ascribed in these solutions.

FIG. 1.



Curves showing influence of inert salt on catalytic activity of hydrochloric (I), *dichloroacetic* (II), *chloroacetic* (III), *and acetic* (IV) *acids in* 0·1N-*solution.*

As a matter of history, it may be recalled that in accordance with the dual theory, values for the catalytic activity of the hydrogen chloride molecule have been derived for various reactions (sucrose inversion, ester hydrolysis, iodination of acetone, etc.), but since all such values were based on degrees of ionisation derived from conductivity and osmotic measurements, they are now devoid of significance. Measurements of the partial pressures of hydrochloric acid solutions (Dunn and Rideal, J., 1924, **125**, 676) and of the distribution of hydrogen chloride between water and benzene (Knight and Hinshelwood, J., 1927, 466) would, indeed, seem to have established the fact that the proportion of hydrogen chloride

molecules in a dilute solution ($<1N$) of hydrochloric acid is extremely small. For many purposes the ionisation of such solutions may be regarded as complete. On the other hand, it must be remembered *that the catalytic activity of undissociated acid molecules increases* rapidly with the strength of the acid, and there is evidence to support the view that undissociated hydrogen chloride is an extremely active catalyst. This activity has been noted repeatedly for reactions in non-aqueous media. The very high speed of the auto-catalysed reaction between acetone and iodine in solvents such as benzene, nitrobenzene and carbon tetrachloride (Dawson and Leslie, J., 1909, **95**, 1860) may also be cited in support of this view. In these circumstances, the possibility that the very small amount of non-ionised hydrogen chloride, which is present in aqueous solutions of the acid, may under certain conditions be partly *responsible for the observed catalytic effect cannot be entirely* ignored. Alternatively, it may be assumed that the observed increase in the catalytic activity of the hydrochloric acid on the addition of salt is entirely due to an inert salt effect in the sense that this increases the magnitude of the catalytic coefficient which is characteristic of the hydrogen ion. If k_x denote this coefficient for an inert salt solution of concentration x, v the corresponding reaction velocity, and c the concentration of the strong acid, then $k_x = v/c$. The value thus obtained for k_x has been adopted as a measure of the coefficient for the hydrogen ion in the corresponding salt solutions of the weak acids. In connexion with this procedure, it may be pointed out that it is not of primary importance to know whether the difference between k_x and the corresponding value k_0 for a salt-free solution is due to the stimulating action of the inert salt on the hydrogen ion or to a minute quantity of the highly active undissociated strong acid. It is possible that both effects are involved.

When the relative velocity curves in Fig. 1 are compared, one is forced to the conclusion that the inert salt effects shown by the weaker acids involve some factor which is practically ineffective in the case of the strong acid. As will be shown presently, there is reason to believe that this factor is represented by a change in the ionisation constant of the acid.

Before proceeding to describe the results obtained in connexion with this view, it should be mentioned that the study of the catalytic effects produced by *acetic acid–acetate mixtures represented* by the general formula $0{\cdot}1CH_3{\cdot}CO_2H + yCH_3{\cdot}CO_2Na$ in sodium chloride solutions, has shown that the relations are closely similar to those which are afforded by the same mixtures in pure aqueous solution. As the concentration of the sodium acetate increases,

the velocity falls to a minimum and subsequently increases with y in a linear manner. From these results it has been possible to derive the values of the catalytic coefficients which characterise the acetate ion and the undissociated acetic acid in the inert salt solutions. For our present purpose, it is sufficient to note that the value of k_m for acetic acid is practically the same for sodium chloride solutions as for pure water, *viz.*, $k_m = 1{\cdot}5 \times 10^{-6}$.

In conformity with previous results the reaction velocity for the mixture $c\mathrm{CH_3{\cdot}CO_2H} + x\mathrm{NaCl}$ may be written

$$v = k_x[\mathrm{H^+}] + k_a[\mathrm{A^-}] + k_m[\mathrm{HA}] \quad . \quad . \quad . \quad . \quad (1)$$
$$= (k_x + k_a - k_m)[\mathrm{H^+}] + k_m c$$

and since k_a and k_m are very small compared with k_x

$$v = k_x[\mathrm{H^+}] + k_m c \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since v, k_x, k_m, and c are known, this equation may be utilised for the derivation of the concentration of the hydrogen ion resulting

TABLE II.

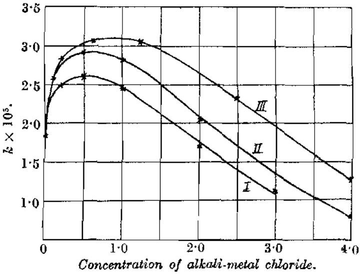
x.	$v \cdot 10^6$.	$k_x \cdot 10^4$.	$[\mathrm{H^+}] \cdot 10^3$.	$K \cdot 10^5$.
		Potassium chloride.		
0	0·777	4·65	1·35	1·82
0·2	0·919	4·88	1·58	2·50
0·5	0·990	5·23	1·61	2·59
1·0	1·052	5·82	1·56	2·43
2·0	1·056	6·99	1·30	1·69
3·0	1·040	8·30	1·07	1·15
		Sodium chloride.		
0·2	0·975	4·91	1·68	2·82
0·5	1·055	5·30	1·71	2·91
1·0	1·143	5·95	1·67	2·79
2·0	1·18	7·26	1·42	2·02
4·0	1·165	11·10	0·91	0·84
		Lithium chloride.		
0·125	0·924	4·83	1·60	2·57
0·625	1·115	5·50	1·75	3·06
1·25	1·26	6·36	1·74	3·04
2·5	1·39	8·07	1·54	2·36
4·0	1·39	11·0	1·13	1·27
		Potassium nitrate.		
0·05	0·867	4·60	1·53	2·33
0·1	0·895	4·73	1·58	2·48
0·5	0·985	5·04	1·66	2·74
1·0	1·007	5·43	1·58	2·48
2·0	0·955	6·20	1·30	1·69
		Sodium nitrate.		
0·1	0·923	4·74	1·63	2·66
0·5	1·025	5·11	1·71	2·93
1·0	1·06	5·57	1·635	2·67
2·0	1·07	6·48	1·42	2·02
4·0	1·03	8·30	1·035	1·07

rom the ionisation of the acetic acid in the inert salt solution. The corresponding value of the ionisation constant is then given by

$$K = [H^+]^2/(c - [H^+]) = (v - k_m c)^2/k_x^2 c \quad . \quad . \quad (3)$$

Table II records the values obtained in this way from the data for $0{\cdot}1N$-acetic acid solutions. Col. 1 gives the concentration x of the inert salt, col. 2 the observed reaction velocity v, col. 3 the value of k_x derived from the corresponding experiments with $0{\cdot}1N$-hydrochloric acid as catalyst, col. 4 the calculated hydrogen-ion concentration, and col. 5 the corresponding ionisation constant. From the tabulated values of K it is apparent that the addition of gradually increasing quantities of inert salt is associated in the

FIG. 2.



Curves showing the variation of the ionisation constant of acetic acid in solutions of potassium (I), *sodium* (II), *and lithium* (III) *chlorides.*

first instance with an increase in the ionisation constant of the acetic acid; the ionisation, however, reaches a maximum and shows a marked fall in the more concentrated salt solutions. For the strongest salt solutions, the value of K is, indeed, much smaller than for the salt-free acid solution.

The relations between the effects produced by potassium, sodium, and lithium chlorides are shown by Fig. 2, in which K is plotted against the molar salt concentration. These curves are clearly similar to those obtained by Harned (*loc. cit.*) for the influence of the three chlorides on the ionisation of water. In both cases, the maximum value for the ionisation constant is greatest for the lithium and least for the potassium chloride solutions, and it would appear that the effectiveness of the factor which is responsible for the fall in the ionisation constant is greatest for the potassium

and least for the lithium salt. Harned's data are based on potentiometric measurements of the thermodynamic activity of the hydrogen ion in salt solutions, and the similarity between the two sets of results would seem to suggest some connexion between the thermodynamic activity and the catalytic activity of the hydrogen ion. We are not, however, prepared to draw any general conclusions from the similarity of the curves.

So far as our own results are concerned, they seem to afford substantial evidence for the view that the ionisation constants of the weak acids are appreciably affected by the addition of salts to the aqueous solutions of the acids. It does not appear possible to refer these variations entirely to changes in the dielectric capacity of the solvent medium. The nature of the variations would rather suggest that attention must be directed to the localised interactions between the molecules of the weak electrolyte and the ions of the salt. These molecules are of the polar type, and on the average the positive poles will be in closer proximity to the negative ions than to the positive ions. In the same way, the negative poles of the dissociable molecules will be nearer on the average to the positive ions than to the negative ions. The polar molecules will thus be subjected to forces which increase the tendency to ionisation. This effect may be expected to increase at first with the number of the ions which are present per unit of volume, but it seems probable that the influence of individual ions will ultimately be overshadowed by that due to the whole group of positive and negative ions which are within range of the poles of the ionisable molecule, and in the limit it would seem that the dielectric capacity of the surrounding medium will be the chief factor which determines the degree of ionisation of the weak electrolyte. This hypothesis would seem to afford a qualitative explanation of the ionisation curves in Fig. 2.

That the results obtained with acetic acid are not peculiar to this acid may be seen by reference to Table III in which are recorded the corresponding data derived from experiments with $0{\cdot}1N$-chloroacetic acid. Since the catalytic activity of the chloroacetate ion is negligibly small, the equation for the velocity of reaction may be written

$$v = (k_x - k_m) \, . \, [H^+] + k_m c \quad . \quad . \quad . \quad . \quad (4)$$

Experiments with chloroacetic acid–sodium chloroacetate mixtures in sodium chloride solutions have shown that the value of k_m varies but slightly with the concentration of the inert salt, and $k_m = 22 \times 10^{-6}$ has been taken as the mean value of the catalytic coefficient for the chloroacetic acid molecule in the calculation of $[H^+]$ and of the corresponding value of K.

TABLE III.

Ionisation of Chloroacetic Acid in Sodium Chloride Solutions.

x.	$v \cdot 10^6$.	$k_x \cdot 10^4$.	$[H^+] \cdot 10^2$.	$K \cdot 10^3$.
0	7·28	4·65	1·15	1·49
0·1	8·06	4·78	1·285	1·90
0·2	8·56	4·91	1·355	2·13
0·5	9·30	5·30	1·40	2·28
1·0	10·1	5·95	1·38	2·20
2·0	11·2	7·26	1·28	1·87
4·0	12·0	11·1	0·90	0·89

As in the case of acetic acid, the ionisation constant of chloroacetic acid first increases and then decreases as the concentration of the sodium chloride increases. The salt concentrations which correspond with the respective maximum values of the ionisation constants are approximately the same for the two acids. The ratios between the maximum values and the values for pure water are also approximately the same. The available material is, however, insufficient to permit of the conclusion that the effect is independent of the strength of the acid.

In conclusion, it may be pointed out that inert salt effects such as are described in this paper must play some part in all acid-catalysed reactions which take place in the presence of salts. In so far as the kinetic studies described in previous papers of this series are concerned, the inert salt effects are, however, not of any great significance, and the general conclusions which have been drawn from the experiments with mixtures of weak acids and their corresponding salts are not affected thereby.

Summary.

Measurements have been made of the velocity of the acetone–iodine reaction when catalysed by hydrochloric, dichloroacetic, monochloroacetic, and acetic acids in solutions of sodium chloride (0—4 molar).

The nature of the influence of the catalytically inert sodium chloride varies with the strength of the acid.

On the assumption that the increase in the reaction velocity produced by the addition of inert salts to a strong acid (hydrochloric acid) is due to a change in the catalytic activity of the hydrogen ion, it is shown that the ionisation constant of a weak acid is first increased by the added salt and then diminished at higher salt concentrations.

Similar variations in the influence of salts on the ionisation of water are indicated by *E.M.F.* measurements.

The general conclusions drawn from the study of the catalytic properties of mixtures of weak acids and the corresponding salts are not affected by the inert salt effects described in this paper.

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CLXII.—*Acid and Salt Effects in Catalysed Reactions. Part XIV. The Influence of Inert Salts on the Catalytic Catenary for Acetic Acid–Acetate Mixtures.*

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IN the preceding paper experiments were described which show *that the catalytic effects produced by acetic acid in the acetone-iodine reaction are appreciably modified by the addition of sodium chloride or other catalytically inert salts to the pure acid solution.* Small quantities of inert salt increase the reaction velocity, but as the concentration is further augmented the velocity attains a maximum and then decreases. In explanation of these results, it has been suggested that there are two distinct effects which are involved in the action of the inert salt. The first is represented by an increase in the catalytic activity of the hydrogen ion, and the second by a change in the ionisation constant of the acid. The former increases continuously with the salt concentration, whilst *the ionisation constant increases to a maximum value and then decreases.*

The object of the present paper is to show that the inert-salt effects referred to above do not modify to any marked extent the character of the relations which are exhibited by the reaction velocities for the acid–salt mixtures which have been investigated in previous experiments. For mixtures of the type cHA + xMA, where HA is a weak acid, c is constant, and x is variable, it has been shown that the reaction velocity in aqueous solution is a function of the hydrogen-ion concentration such that the plot of v against $\log [H^+]$ is represented by a catenary curve. The experiments *now described show that the relations are unaltered when inert-salt solutions are substituted for water as the medium in which the catalysed reaction takes place.*

The salt solutions used were 0·1, 0·5, 2·0, and 4·0M-solutions of sodium chloride, and the active catalytic mixtures were those represented by the formula $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$. In all the solvents the reaction velocity falls rapidly to a minimum and

subsequently increases in a linear manner as the concentration of the acetate is continuously increased. So far as the empirical relations between v and x are concerned, there is no essential difference between the results obtained with water and those with the various sodium chloride solutions. In all cases, the catalytic properties of the group of acetic acid–acetate mixtures can be expressed in terms of an equation of the form *

$$v = k_h[H^+] + k_a[A^-] + k_m[HA] \quad . \quad . \quad . \quad . \quad (1)$$

and such differences as are found are, for the most part, to be attributed to changes produced by the inert salt in the magnitudes of the catalytic coefficients k_h, k_a, and k_m, and of the ionisation constant of the acetic acid. These changes modify to some extent the hydrogen-ion concentration and the minimum reaction velocity which characterise the isocatalytic point, but the general relations which find expression in the catalytic catenary are not affected.

The calculation of reaction velocities from equation (1) presumes a knowledge of the values of k_h, k_a, and k_m and of the ionisation constant K. It will be assumed that k_h for the various solvents is given by the reaction velocities obtained with hydrochloric acid as catalyst (compare Dawson and Key, *loc. cit.*). The values of k_a and k_m may be obtained by the method described by Dawson and Carter (J., 1926, 2282), according to which k_a is given by the slope of the v–x line, and k_m by extrapolation of this line to $x = 0$. In this procedure, an error in the determination of k_a will, however, affect the value obtained for k_m. For this reason, a method has been adopted for the evaluation of k_m in which k_a plays no essential part. This consists in determining the reaction velocities for varying concentrations of acetic acid in acetate-free solutions. If c denotes the concentration of the acid, equation (1) may be written

$$v = (k_h + k_a - k_m)[H^+] + k_m c \quad . \quad . \quad . \quad (2)$$

and since $k_a - k_m$ can be neglected by comparison with k_h, and $[H^+]$ is given approximately by $\sqrt{Kc}$ when c is not too small, this equation may be put in the form

$$v/\sqrt{c} = k_h\sqrt{K} + k_m\sqrt{c} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

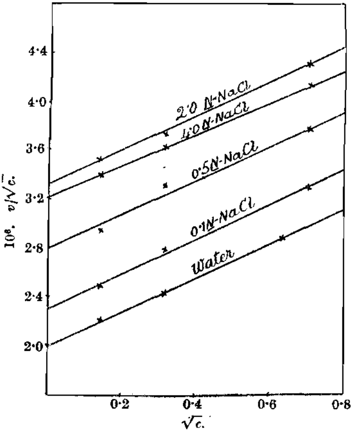
According to equation (3), the plot of $v/\sqrt{c}$ against $\sqrt{c}$ should yield a straight line of slope k_m intersecting the ordinate ($c = 0$) at a point which affords a measure of $k_h\sqrt{K}$. In actual fact, the experimental data for 0·02, 0·1, and 0·5M-solutions of acetic acid

* It has been shown that the water molecule has a measurable activity (Dawson and Key, this vol., p. 543). The effect in question is very small and in this paper it is not specifically taken into account, but may be supposed to be included in the term which corresponds with the undissociated acetic acid.

are in close agreement with the requirements of equation (3), and as Fig. 1 shows, the lines for water and for the 0·1, 0·5 and 2·0*M*-sodium chloride solutions are very nearly parallel, with the common value $k_m = 1{\cdot}4 \times 10^{-6}$. The slope of the line for the 4·0*M*-chloride solutions is somewhat less and corresponds with $k_m = 1{\cdot}3 \times 10^{-6}$. These observations show clearly that the catalytic activity of the acetic acid molecule is scarcely affected by the inert salt, even when this is present in large quantity.

FIG. 1.

Graph of $v/\sqrt{c}$ against $\sqrt{c}$ for acetic acid as catalyst in water and sodium chloride solutions.



Since the linear portion of the v–x curves for the mixtures of the series $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$ can be expressed by the equation $v = 0{\cdot}1k_m + k_a x$, it is obvious that this may be used to determine the values of k_a. In the actual experiments with such mixtures, it was found expedient to limit the concentration of the acetate to values not greater than 0·4 mol. per litre. This limitation is necessitated by the circumstance that the iodoacetone which is formed in the first stage of the reaction begins to react at an appreciable rate with a further quantity of iodine, and thus tends to disturb the measurement of the velocity of the primary change.

he k_a values derived in this way are shown in col. 3 of Table I, nd it is apparent that the influence of the inert salt on the magitude of the coefficient which measures the catalytic activity of the cetic ion is also comparatively slight.

Col. 4 of Table I shows the values of $k_h\sqrt{K}$ which are given by he intercepts of the $v/\sqrt{c}$–$\sqrt{c}$ lines in Fig. 1 on the zero ordinate. f these are divided by the corresponding values of k_h (col. 5) given y the reaction-velocity data with hydrochloric acid as catalyst, e obtain $\sqrt{K}$. The squares of these are tabulated under K in ol. 6, and these numbers represent the values of the ionisation onstant of the acid in the various solutions.

TABLE I.

atalytic Constants for Acetic Acid in Sodium Chloride Solutions.

Reaction Medium.	$k_m \cdot 10^6$.	$k_a \cdot 10^6$.	$k_h \cdot \sqrt{K} \cdot 10^6$.	$k_h \cdot 10^6$.	$K \cdot 10^5$.
Vater	1·4	4·0	2·00	465	1·85
·1N-NaCl	1·4	4·0	2·30	478	2·31
·5N-NaCl	1·4	3·7	2·80	530	2·79
·0N-NaCl	1·4	3·4	3·32	726	2·09
·0N-NaCl	1·3	3·4	3·22	1110	0·84

t may be noted that the values of k_m are but slightly different from he value $1·5 \times 10^{-6}$ assigned to the acetic acid molecule in 1913 y Dawson and Powis (J., **103**, 2135). The k_a value for the pure queous solution is definitely smaller than that recorded by Dawson nd Carter (*loc. cit.*), namely, $k_a = 4·5 \times 10^{-6}$, but the higher value s in all probability due to the less complete elimination of the listurbing effect of subsequent reactions in the case of the solutions vhich contain relatively large amounts of acetate.

The slight variation of the k_m and k_a values with the solvent is n marked contrast to the relatively large changes in k_h and K. The variations of K correspond closely with those shown by the igures recorded in Table II of the previous paper. The latter were lerived by a somewhat different procedure, but both methods nvolve the assumption that the reaction-velocity data for hydrohloric acid in the several sodium chloride solutions afford a measure f the catalytic activity of the hydrogen ion. The possibility that k_h determined in this way includes some factor other than that epresented by the influence of the inert salt on the catalytic activity f the ion has already been discussed. It might be suggested that his view receives some support from the relations which are dislosed by the foregoing table, but it does not seem possible to carry he matter further at the present time.

Table II affords a comparison of the reaction velocities observed vith free acetic acid in the various solvents and those calculated

from equation (2) by means of the constants recorded in Table I. The required hydrogen-ion concentrations are those derived from $[H^+] = \sqrt{K(c - [H^+])}$. It is apparent that the differences between the observed and calculated reaction velocities for the pure acetic acid solutions are not greater than would be accounted for by experimental error.

TABLE II.

Catalyst: Acetic Acid. Temp.: 25°.

Solvent.	$c = 0{\cdot}02$. $v.10^6$ (obs.).	$c = 0{\cdot}02$. $v.10^6$ (calc.).	$c = 0{\cdot}1$. $v.10^6$ (obs.).	$c = 0{\cdot}1$. $v.10^6$ (calc.).	$c = 0{\cdot}5$. $v.10^6$ (obs.).	$c = 0{\cdot}5$. $v.10^6$ (calc.).
Water	0·312	0·308	0·770	0·772	1·82	1·83
0·1*N*-NaCl ...	0·350	0·349	0·883	0·866	2·33	2·33
0·5*N*-NaCl ...	0·412	0·418	1·055	1·025	2·67	2·68
2·0*N*-NaCl ...	0·500	0·491	1·175	1·185	3·05	3·04
4·0*N*-NaCl ...	0·480	0·477	1·150	1·145	2·92	2·92

The observed and calculated velocities for the constant-acid series of mixtures are compared in the same way in Table III. The calculated velocities are derived from equation (1) in which $[H^+]$, $[A^-]$, and [HA] are given by $[H^+] = K(c - [H^+])/(x + [H^+])$, $[A^-] = x + [H^+]$, and $[HA] = c - [H^+]$, respectively. The result

TABLE III.

Catalyst: $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$. Temp.: 25°.

$x =$	0	0·005	0·01	0·02	0·03	0·05	0·1	0·2	0·4
Solvent: water.									
$v.10^6$ (obs.)	0·770	0·333	0·276	0·276	0·297	0·365	0·570	0·930	1·71
$v.10^6$ (calc.)	0·772	0·321	0·265	0·263	0·289	0·357	0·548	0·944	1·74
Solvent: 0·1*N*-NaCl.									
$v.10^6$ (obs.)	0·883	0·385	0·304	0·282	0·301	0·363	0·549	0·938	1·74
$v.10^6$ (calc.)	0·866	0·359	0·289	0·274	0·297	0·362	0·551	0·946	1·74
Solvent: 0·5*N*-NaCl.									
$v.10^6$ (obs.)	1·055	0·434	0·320	0·290	0·311	0·368	0·547	0·910	1·63
$v.10^6$ (calc.)	1·025	0·428	0·321	0·287	0·300	0·355	0·525	0·888	1·62
Solvent: 2·0*N*-NaCl.									
$v.10^6$ (obs.)	1·175	0·415	0·311	0·277	0·290	0·340	0·512	0·845	1·53
$v.10^6$ (calc.)	1·185	0·438	0·323	0·283	0·292	0·340	0·495	0·828	1·50
Solvent: 4·0*N*-NaCl.									
$v.10^6$ (obs.)	1·150	—	0·261	0·237	0·253	0·296	0·472	0·785	1·50
$v.10^6$ (calc.)	1·145	—	0·256	0·244	0·263	0·319	0·479	0·814	1·47

show that the reaction velocities in water and in the sodiu chloride solutions are closely reproduced by an equation whic takes account of the catalytic effects produced respectively by tl hydrogen ion, the acetic ion, and the undissociated acetic aci molecule. By slight modifications of the values assigned to

and k_m in Table I, it might be possible to bring the calculated numbers into closer agreement with the observed velocity, but this does not seem necessary, for the main object of these experiments is to show that the presence of inert salts makes no difference to the general character of the results which are obtained for mixtures of a weak acid and the corresponding salt.

Since the v–log $[H^+]$ curve for such mixtures with constant acid concentration is a catenary, it follows that the plot of the reaction velocity against log x should also yield a catenary curve, for $[H^+]$ is inversely proportional to x provided that the acetate concentration is not too small. The v–log x curve has, for certain purposes, an obvious advantage over the v–p_H curve in that it involves the correlation of the directly measured quantities v and x. When the data recorded in Table III are plotted in this way, a series of catenary curves is obtained. The symmetry of these curves facilitates the determination of the minimum reaction velocity v_i and the acetate concentration x_i which correspond with the respective isocatalytic points. From x_i, the value of $[H^+]_i$ is given by $[H^+]_i = 0{\cdot}1K/x_i$, where K is the ionisation constant of the acetic acid in the solvent concerned.

The observed minimum velocities are shown in col. 2 of Table IV, whilst the calculated velocities derived from the equation

$$v_i = 2\sqrt{(k_h - k_m)k_aKc} + k_mc \quad . \quad . \quad . \quad . \quad (4)$$

are shown in col. 3. Col. 4 gives the values of the acetate concentration at the *M.V.* point, and col. 5 the corresponding values of $(p_H)_i$. The calculated values of $(p_H)_i$ in col. 6 are those which follow from the general equation

$$[H^+]_i = \sqrt{k_aKc/(k_h - k_m)} \text{ or } (p_H)_i = \tfrac{1}{2}\{\log(k_h - k_m) - \log k_aKc\} \quad (5)$$

For the derivation of these equations reference may be made to Part II (Dawson and Dean, J., 1926, 2872).

TABLE IV.

Isocatalytic data for $0{\cdot}1CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$.

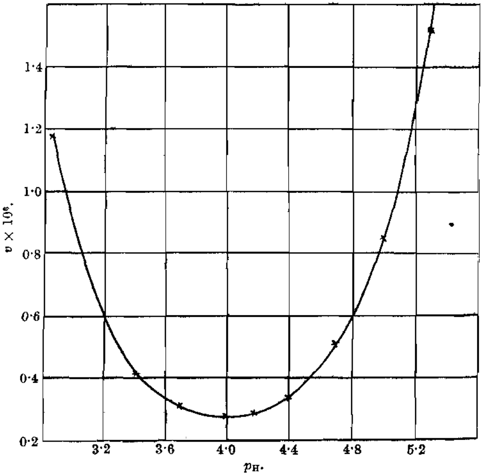
Solvent.	v_i . 10^6 (obs.).	v_i . 10^6 (calc.).	x_i.	$(p_H)_i$ (obs.).	$(p_H)_i$ (calc.).
Water	0·267	0·256	0·0165	3·95	3·90
0·1*N*-NaCl	0·278	0·277	0·0175	3·88	3·86
0·5*N*-NaCl	0·288	0·288	0·0190	3·83	3·85
2·0*N*-NaCl	0·280	0·283	0·0205	3·99	4·00
4·0*N*-NaCl	0·237	0·243	0·0190	4·35	4·30

In reference to the above table it may be noted that the quantity of sodium acetate which is required to reduce the catalytic activity to a minimum increases with the concentration of the inert salt, reaches a maximum and then diminishes. In general, the agree-

ment between the observed and calculated isocatalytic data is sufficient to indicate the applicability of the theory to all the solvents investigated, but it may be noted that the greatest difference between the observed and calculated minimum velocities is shown by the data for water as solvent. It is probable that this is connected with the inert-salt action of the sodium acetate, for in the absence of sodium chloride this may be expected to produce a

FIG. 2.

Catalytic catenary (v–p_H) *for* $0{\cdot}1N$-$CH_3{\cdot}CO_2H + xCH_3{\cdot}CO_2Na$ *in a solution of* 2·0M-*sodium chloride*.



greater effect than in those solutions which already contain sodium chloride. It has indeed been shown that the inert-salt effect, as measured by $dv/d[NaCl]$, diminishes with increase in the concentration of the inert salt and ultimately becomes negative (compare Dawson and Key, *loc. cit.*). The fact that the observed value of v_i for the pure aqueous solvent is greater than the calculated value, accords completely with this view in the sense that the addition of acetate to the salt-free solution should correspond with an increase in the ionisation constant of the acid. There is reason to believe,

however, that the inert-salt effect produced by the sodium acetate will not be so large as that produced by an equivalent amount of sodium chloride.

In Fig. 2 the observed reaction velocities for $2N$-sodium chloride as solvent are plotted against the p_H values *derived in the usual* way from the value of K tabulated for this solvent in Table I, *viz.*, $K = 2{\cdot}09 \times 10^{-5}$. The symmetrical catenary distribution of the points is obvious. In this connexion, it is of interest to compare the p_H values of the pure acid solutions with the p_H values of the acetic–acetate mixtures which exhibit the same catalytic activity as the acetate-free solutions. The concentration of the acetate (x_c) for such mixtures can be read off directly from the v–x curves. The corresponding hydrogen-ion concentration is given by $[H^+]_c = 0{\cdot}1K/x_c$. If $[H^+]_0$, derived from $[H_0^+] = \sqrt{0{\cdot}1K}$, represents the hydrogen-ion concentration of the acetate-free solution, we have, as previously shown,

$$[H^+]_0 \,.\, [H^+]_c = [H^+]_i^2$$

or

$$(p_H)_i = \tfrac{1}{2}\{(p_H)_0 + (p_H)_c\}$$

In Table V, col. 2 gives the values of x_c, cols. 3 and 4 the values of $(p_H)_0$ and $(p_H)_c$, col. 5 the arithmetic mean of these, and col. 6 the value of $(p_H)_i$ derived by calculation from equation (5).

TABLE V.

Symmetry of the Catalytic Catenaries.

Solvent.	x_c.	$(p_H)_0$.	$(p_H)_c$.	$\frac{(p_H)_0+(p_H)_c}{2}$.	$(p_H)_i$.
Water	0·16	2·86	4·94	3·90	3·90
$0{\cdot}1N$-NaCl	0·184	2·82	4·90	3·86	3·86
$0{\cdot}5N$-NaCl	0·24	2·78	4·93	3·86	3·85
$2{\cdot}0N$-NaCl	0·292	2·84	5·15	4·00	4·00
$4{\cdot}0N$-NaCl	0·310	3·04	5·57	4·30	4·30

The almost complete identity of the figures in the last two columns may be to some extent fortuitous, but when due allowance is made for this, the results must be regarded as affording strong evidence for the view that the presence of sodium chloride does not affect the nature of the relations which find expression in the symmetrical catenary curves. The main object with which this series of experiments was planned has thus been attained. This was to show that the catalytic phenomena described and co-ordinated in earlier papers of this series are not effects which can be explained in terms of those environmental factors which are associated with the concept of "activity" in its application to solutions of electrolytes. It is true that inert-salt effects may in certain circumstances play an important part in modifying the velocities of acid-catalysed reactions,

This is the case, for instance, when inert salts are added to a salt-free solution of a weak electrolyte, and the conditions are such that any change in the degree of ionisation of the catalysing acid is reflected in a corresponding change in the reaction velocity. On the other hand, it is equally clear that when these particular conditions do not obtain, the importance of such inert-salt effects may be relatively small and entirely insufficient to affect the general nature of the results which are conveniently expressed in terms of the catalytic catenary. It may indeed be anticipated that the generalised catalytic equation $r = \cosh \log_e n$, which expresses the connexion between the reduced ionic velocity r and the reduced hydrogen-ion concentration n, will be applicable with greater precision to salt-containing solutions than it is to solutions which are free from catalytically inert salts.

In conclusion, attention may be directed to the circumstance that equation (3) may be derived from a comparison of the equations *for the velocity* (v_0) *of the salt-free acid solution and for the velocity* (v_e) of the catalytically conjugate acid–salt mixture $cHA + x_eMA$. We have

$$v_0 = k_h[H^+]_0 + k_m c = k_h\sqrt{Kc} + k_m c$$
$$v_e = k_a x_e + k_m c$$

and since $v_0 = v_e$, we obtain

$$k_h\sqrt{Kc} = k_a x_c = v_e - k_m c = v_0 - k_m c$$

or

$$k_h\sqrt{K} = v_0/\sqrt{c} - k_m\sqrt{c}$$

*which is the same as the relation previously derived from a con*sideration of the catalytic effects prodnced by the pure acid at different concentrations. From $k_h\sqrt{Kc} = k_a x_e$, we derive $K = (k_a x_e/k_h)^2/c$. If the tabulated values of k_a, k_b, and x_e are substituted in this eqnation, we obtain K = 1·89, 2·36, 2·93, 1·87, and 0·90 for the series of five solvents examined. These differ somewhat from the K values recorded in Table I, but show the same general relations.

Summary.

The influence of catalytically inert salts on the velocity of the acetone–iodine reaction has been examined when the reaction is catalysed by a weak acid in the presence and in the absence of the corresponding salt.

The relations in sodium chloride solutions (0·1 to 4·0 molar) are closely similar to those which are exhibited by pure aqueous solutions

The coefficients which measure the catalytic activity of the acetic acid molecule and of the acetate ion are but slightly affected by the presence of sodium chloride. On the other hand, it would seem that

the catalytic activity of the hydrogen ion and the degree of ionisation of acetic acid vary considerably with the salt concentration.

The v–p_H curves approximate in all cases to a true catenary. The isocatalytic data vary with the salt concentration, but the variations are small.

The results show that the catalytic phenomena described and co-ordinated in previons papers are not affected to any great extent by the changes in ionic environment which are associated with the replacement of water as the solvent by solutions of catalytically inert salts.

THE UNIVERSITY, LEEDS. [*Received, March 20th*, 1928.]

CLXIII.—*Reactions of Carbohydrazide. Part II.*

By ANDREW MILLER MUNRO and FORSYTH JAMES WILSON.

THE view expressed in Part I (J., 1927, 107) that in the thermal decomposition which carbohydrazones (or δ-aminosemicarbazones) undergo at their melting points the hydrazidicarbohydrazone (or hydrazidicarbohydrazide itself) is the intermediate product has been confirmed by investigating the thermal decomposition of dibenzaldehydehydrazidicarbohydrazone, *diacetonehydrazidicarbohydrazone*, and hydrazidicarbohydrazide. The decomposition of diacetonecarbohydrazone and *dipinacolincarbohydrazone* both in boiling alcoholic solution and at the melting point has also been found to conform to the general scheme.

The interaction of ethyl acetoacetate and carbohydrazide was next investigated. There are several possibilities:

(*a*) $COMe{\cdot}CH_2{\cdot}CO_2Et + CO(NH{\cdot}NH_2)_2 \xrightarrow[(-H_2O)]{} \begin{matrix} CMe{\cdot}CH_2{\cdot}CO_2Et \\ \| \\ N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2 \end{matrix}$

(I.) *Ethyl acetoacetate δ-aminosemicarbazone.*

or $\xrightarrow[(-H_2O,\ -EtOH)]{} \begin{matrix} CMe{\cdot}CH_2{\cdot}CO \\ N\text{———}N{\cdot}CO{\cdot}NH{\cdot}NH_2 \end{matrix}$ (II.)

(*b*) $2COMe{\cdot}CH_2{\cdot}CO_2Et + CO(NH{\cdot}NH_2)_2 \xrightarrow[(-2H_2O)]{}$
$CO(NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO_2Et)_2$

(III.) *Di(ethyl acetoacetate)carbohydrazone.*

or $\xrightarrow[(-2H_2O,\ -2EtOH)]{} \begin{matrix} CMe{\cdot}CH_2{\cdot}CO \quad CO{\cdot}CH_2{\cdot}CMe \\ N\text{———}N{\cdot}CO{\cdot}N\text{———}N \end{matrix}$

(IV.) 3 : 3′-*Dimethyl*-5 : 5′-*dipyrazolonyl* 1 : 1′-*ketone.*

or $\xrightarrow[(-2H_2O,\ -EtOH)]{} \begin{matrix} CMe{\cdot}CH_2{\cdot}CO \\ N\text{———}N{\cdot}CO{\cdot}NH{\cdot}N{:}CMe{\cdot}CH_2{\cdot}CO_2Et \end{matrix}$

(V.) 3-*Methyl-5-pyrazolone-1-carboxy-α-carbethoxy-isopropylidenehydrazide.*

Of these substances (I), (III), (IV) and (V) were actually obtained. (I) was produced by heating the reactants in equimolecular quantities in alcoholic solution; (III) and (V) were formed together by heating 2 mols. of the ester with 1 mol. of carbohydrazide. On one occasion repetition of the latter experiment gave substances (III) and (IV), (V) not being produced.

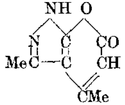
The thermal decomposition of (I) and (III) conformed to the general scheme described in Part I: the amount of (V) did not permit of detailed investigation.

In boiling alcoholic solution (I) yielded hydrazine and *di(ethyl acetoacetate)hydrazidicarbohydrazone* (VI),

$$2CMe(:N\cdot NH\cdot CO\cdot NH\cdot NH_2)\cdot CH_2\cdot CO_2Et = N_2H_4 + [CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)\cdot NH\cdot]_2 \quad \text{(VI.)}$$

On heating at the melting point, (I) gave hydrazine, 4-aminourazole, and 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone (VII) (Bülow and Lobeck, *Ber.*, 1907, **40**, 708; Bülow and Schaub, *Ber.*, 1908, **41**, 1945; Wolff and Schreiner, *ibid.*, p. 550), a decomposition product of ethyl acetoacetate azine, the reaction evidently following the course:

$$2\ (I) = N_2H_4 + (VI) \longrightarrow CO\Big<{N(NH_2) \atop NH\cdot NH}\Big>CO + [N(:CMe\cdot CH_2\cdot CO_2Et)]_2 \longrightarrow$$

2EtOH +  (VII.)

On prolonged boiling in alcoholic solution, (III) gave di(ethyl acetoacetate)hydrazidicarbohydrazone and (VII),

$$2CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)_2 = [CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)\cdot NH\cdot]_2 + (VII) + EtOH;$$

on heating at the melting point, the products were 4-aminourazole and (VII),

$$2CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)_2 = EtOH + (VII) + [CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)\cdot NH]_2 \longrightarrow CO\Big<{N(NH_2) \atop NH\cdot NH}\Big>CO + (VII) + EtOH.$$

EXPERIMENTAL.

Dibenzaldehydehydrazidicarbohydrazone was heated at 250° for 3 hours. Treatment of the cooled powdered mass with ether

extracted benzylideneazine; the residue after recrystallisation from aqueous alcohol proved to be 4-aminourazole.

Hydrazidicarbohydrazide (Stollé, *Ber.*, 1910, **43**, 2468) on heating at 250° for 3 hours gave a distillate which contained hydrazine; the residue, after being washed with ether and recrystallised from aqueous alcohol, was shown to be 4-aminourazole.

Diacetonecarbohydrazone was boiled in absolute alcoholic solution for 30 hours, and the alcohol then distilled off. The residue, after being washed with ether and recrystallised from alcohol, furnished colourless crystals of *diacetonehydrazidicarbohydrazone*, m. p. 256° (Found: N, 36·8. $C_8H_{16}O_2N_8$ requires N, 36·8%). The alcoholic distillate on heating with dilute hydrochloric acid and evaporation gave hydrazine hydrochloride.

The carbohydrazone on heating at 200° for 3 hours gave a distillate of dimethylketazine (b. p. 131°); the residue after the usual treatment proved to be 4-aminourazole.

Diacetonehydrazidicarbohydrazone, identical with the specimen described above, was also obtained by refluxing acetone with hydrazidicarbohydrazide for 1 hour and recrystallising the product from alcohol. On heating at its melting point, it gave dimethylketazine and 4-aminourazole.

Dipinacolincarbohydrazone was prepared by refluxing pinacolin (9·8 g.) with carbohydrazide (4·5 g.) in absolute alcohol (20 c.c.) for 5 hours. On cooling, it separated in small plates, m. p. 188° after recrystallisation from alcohol (Found: C, 61·5; H, 10·3; N, 22·1. $C_{13}H_{26}ON_4$ requires C, 61·4; H, 10·2; N, 22·0%). An alcoholic solution, after boiling for 24 hours, deposited, on cooling, *dipinacolinhydrazidicarbohydrazone*, $(CMe_3{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot})_2$, a white powder, m. p. 230° after recrystallisation from alcohol (Found: N, 26·9. $C_{14}H_{28}O_2N_6$ requires N, 26·9%). The alcoholic solution on evaporation left a resin, from which ether extracted pinacolinazine identical with the specimen previously obtained by one of us (J., 1927, 2116). The carbohydrazone was heated for 1 hour at 250° under reduced pressure. Pinacolinazine distilled over; the residue after the usual treatment was found to be 4-aminourazole.

Dipinacolinhydrazidicarbohydrazone, identical with the specimen described above, was also obtained by refluxing hydrazidicarbohydrazide with excess of pinacolin in alcohol for 10 hours. The dark brown solution after treatment with charcoal and concentration deposited plates which crystallised from alcohol and melted at 230°. The substance on heating at 250° under reduced pressure gave pinacolinazine and 4-aminourazole.

Ethyl acetoacetate δ-aminosemicarbazone (I) was obtained by refluxing 13 g. of the ester with 9 g. of carbohydrazide in 20 c.c. of

absolute alcohol for 1 hour. The powder which separated on cooling was recrystallised several times from alcohol, plates of a slightly yellowish tinge, m. p. 219°, being obtained. The compound was soluble in alcohol but insoluble in ether and chloroform (Found: C, 41·5; H, 6·9; N, 27·9. $C_7H_{14}O_3N_4$ requires C, 41·6; H, 6·9; N, 27·7%). This substance was boiled for 7 hours in absolute alcohol. On cooling, colourless plates separated. The mother-liquor was distilled and hydrazine was detected in the distillate. The plates after recrystallisation from alcohol melted at 213° and consisted of *di(ethyl acetoacetate)hydrazidicarbohydrazone* (Found: C, 45·1; H, 6·5; N, 22·6. $C_{14}H_{24}O_6N_6$ requires C, 45·1; H, 6·5; N, 22·6%).

The δ-aminosemicarbazone was heated at the melting point in a small distilling flask for 1 hour in carbon dioxide under reduced pressure. A small amount of liquid in which hydrazine was present distilled and a little unaltered substance sublimed. The residue was extracted with ether, leaving 4-aminourazole undissolved; the extract on concentration deposited 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone which, after recrystallisation from alcohol, melted at 245° and was identical with an authentic specimen (Found: C, 58·7; H, 4·9; N, 17·0. Calc.: C, 58·5; H, 4·9; N, 17·1%).

26 G. of ethyl acetoacetate were refluxed with 9 g. of carbohydrazide in 20 c.c. of absolute alcohol for 3½ hours. The deep brown solution slowly deposited a brown, crystalline mass which, after being washed with alcohol, was boiled with alcohol containing charcoal. From the filtered solution, yellow prisms of *di(ethyl aceto-acetate)carbohydrazone* (III) slowly separated, m. p. 196° after recrystallisation (Found: C, 49·6; H, 7·1; N, 17·8. $C_{13}H_{22}O_5N_4$ requires C, 49·7; H, 7·0; N, 17·8%). The residue containing charcoal was extracted with boiling alcohol; the extract on cooling deposited lemon-yellow plates of *3-methyl-5-pyrazolone-*1*-carboxy-α-carbethoxy*iso*propylidenehydrazide* (V), m. p. 230° (decomp.) after recrystallisation (Found: C, 49·4; H, 6·0; N, 20·8. $C_{11}H_{16}O_4N_4$ requires C, 49·3; H, 6·0; N, 20·9%). No other substance was detected in this case. On one occasion there was obtained in addition to di(ethyl acetoacetate)carbohydrazone a substance which was sparingly soluble in alcohol and gave on recrystallisation from this solvent a white powder, m. p. 183°; this was 3 : 3′-*dimethyl-5 : 5′-dipyrazolonyl* 1 : 1′-*ketone* (IV) (Found: C, 48·6, 48·7; H, 4·7, 4·7; N, 25·2, 25·4. $C_9H_{10}O_3N_4$ requires C, 48·6; H, 4·5; N, 25·2%).

After boiling for 12 hours an absolute-alcoholic solution of di(ethyl acetoacetate)carbohydrazone, on cooling, deposited plates, m. p. 213°, consisting of di(ethyl acetoacetate)hydrazidicarbohydrazone as shown by analysis and by comparison with the specimen previously obtained. The mother-liquor on evaporation

gave a residue, from which ether extracted 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone. The carhohydrazone was heated at its melting point for 1 hour; the cold powdered mass was extracted with ether, which dissolved 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone; the insoluble residue was found after the usual treatment to consist of 4-aminourazole.

In conclusion, we wish to thank the Carnegie Trust for the Universities of Scotland for a research grant in aid of this work.

THE ROYAL TECHNICAL COLLEGE,
GLASGOW. [*Received, February 20th, 1928.*]

CLXIV.—*The Complex Salts of β-Methyltrimethylenediamine with Bivalent Platinum.*

By FREDERICK GEORGE MANN.

BIVALENT platinum, of co-ordination number 4, forms complex salts which usually have the uniplanar configuration: there is, however, some evidence that certain such salts have the tetrahedral configuration. For instance, considerations of structure alone make it highly probable that ββ'β''-triaminotriethylamineplatinous di-iodide, $[PtN(CH_2{\cdot}CH_2{\cdot}NH_2)_3]I_2$ (Mann and Pope, *Proc. Roy. Soc.*, 1925, *A*, **109**, 457), has the tetrahedral, rather than the uniplanar, configuration. Bis(triaminopropane-monothiocyanate)platinous dithiocyanate, $[Pt\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HSCN\}_2](SCN)_2$, is identical in type with the corresponding cupric salt (Mann, this vol., p. 890): since the tetrammino-cupric complex is known to have the tetrahedral configuration, it is again highly probable that the platinous salt also has the same configuration. Attempts were made to obtain more decisive evidence by a further study of the salts of the bis(β-methyltrimethylenediamine)platinous complex,

$$\left[\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CH_2{\cdot}NH_2\\CH_2{\cdot}NH_2\end{matrix}\!\!>\!Pt\!<\!\!\begin{matrix}NH_2{\cdot}CH_2\\NH_2{\cdot}CH_2\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CH_3\\H\end{matrix}\right]''$$

(Mann, J., 1927, 2917). If this complex has the uniplanar configuration, its salts should show *cis-trans* isomerism according as the two methyl groups are on the same or opposite sides of the common plane of the two rings: if it has the tetrahedral configuration, the two ring systems are at right angles to each other, and the molecular dissymmetry thus produced should render its salts capable of resolution into optically active forms.

The six salts of this complex which have been isolated showed no sign of *cis-trans* isomerism, although they were all highly crystalline

compounds in which such isomerism should have been readily detected: moreover, their widely differing solubilities make it extremely unlikely that a more soluble isomeride remained in solution in each case, and so avoided identification. The camphorsulphonate, bromocamphorsulphonate, and tartrate, on the other hand, could not be resolved into optically active forms. Such salts, like those of the corresponding nickelous complex (Mann, *loc. cit.*), thus provide no evidence as to the configuration of the metallic complex. If the complex is uniplanar, this may be due to one isomeride being relatively so stable that it is formed to the almost complete exclusion of the other: if the complex is tetrahedral, the absence of evidence may be due to very rapid racemisation of the salts in solution.

Experimental.

All rotations have been measured at 15° in a 4-dcm. polarimeter tube, using the mercury green line ($\lambda = 5461$).

Bis(β-methyltrimethylenediamine)platinous Dichloride, $[Pt\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2]Cl_2$.—A solution of β-methyltrimethylenediamine dihydrochloride (12 g. 3 mols.) in 10% aqueous sodium hydroxide (58 c.c.) was added to a solution of potassium chloroplatinite (10 g.) in water (150 c.c.), and the whole boiled gently under reflux. The red colour of the chloroplatinite rapidly faded, and long, colourless needles separated these slowly redissolved, giving a colourless solution. The latter when concentrated on the water-bath, can be used for the preparation of most salts of the complex.

The dichloride was obtained when the colourless solution was allowed to cool and crystallise: it separated in long, colourless uniform needles, m. p. 266—267° (decomp.).

The *dibromide*, obtained by treating the colourless solution with saturated sodium bromide solution, was recrystallised from water and separated in colourless needles, m. p. 266—268° (decomp. (Found: C, 18·0; H, 4·55; Pt, 36·6. $C_8H_{24}N_4Br_2Pt$ requires C 18·1; H, 4·55; Pt, 36·7%).

The *di-iodide*, similarly obtained by precipitation with potassium iodide, when recrystallised from hot water gave colourless, crystallin leaflets, m. p. 263—264° (decomp.) with preliminary darkenin (Found: C, 15·4; H, 3·9; Pt, 31·2. $C_8H_{24}N_4I_2Pt$ requires C, 15·4 H, 3·9; Pt, 31·2%). The di-iodide, owing to its very slight solubility in cold water, is the best form in which to isolate the comple from the colourless solution obtained in the original preparation.

The *dinitrate*, obtained from the original solution by treatmer with sodium nitrate, separates on recrystallisation from hot wat

in large, dense, colourless crystals, which are only slightly soluble in cold water. On heating, it deflagrates violently (Found : C, 19·2; H, 4·9; Pt, 39·1. $C_8H_{24}O_6N_6Pt$ requires C, 19·4; H, 4·9; Pt, 39·4%).

The *di*-d-*camphor*-β-*sulphonate monohydrate*,

$$[Pt\{CH_3\cdot CH(CH_2\cdot NH_2)_2\}_2](C_{10}H_{15}O\cdot SO_3)_2,H_2O,$$

was obtained by treating the di-iodide in hot aqueous solution with the calculated quantity of silver *d*-camphorsulphonate. The solution, when boiled, filtered, and concentrated, gave the *sulphonate* in fine, colourless crystals, moderately easily soluble in cold water. These were recrystallised three times from water, and then had m. p. 279—281° (decomp.) (Found: C, 39·6; H, 6·6; Pt, 23·2. $C_{28}H_{56}O_9N_4S_2Pt$ requires C, 39·5; H, 6·6; Pt, 22·9%). A 1·467% aqueous solution had $\alpha = +0{\cdot}90°$, $[\alpha] = +15°$, $[M] = +130°$: neither the rotation nor the decomposition point was changed by further recrystallisation from water. Since Graham (J., 1912, **101**, 746) has found the camphorsulphonate ion at similar concentration to have an average value of $[M] = 66°$, the rotation of the above salt must have been due to the sulphonate ions alone: this was confirmed by converting the dicamphorsulphonate into the dibromide, which was inactive.

The *di*-d-α-*bromocamphor*-π-*sulphonate* was prepared by mixing very dilute hot aqueous solutions of the di-iodide and of the calculated quantity of silver *d*-bromocamphorsulphonate: from the filtered, cooled mixture, the very sparingly soluble *di*-d-*bromocamphorsulphonate* separated rapidly in long colourless needles, which on heating decomposed slowly between 278° and 285° (Found: C, 34·0; H, 5·25; Pt, 19·7. $C_{28}H_{52}O_8N_4Br_2S_2Pt$ requires C, 33·9; H, 5·3; Pt, 19·7%). After three recrystallisations of the salt from water, a 0·8453% solution had $\alpha = +2{\cdot}34°$, $[\alpha] = +69{\cdot}2°$, and $[M] = +686°$. Since the bromocamphorsulphonate ion has $[M] = 347°$, the rotation of the complex salt is again due solely to the sulphonate ions.

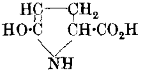
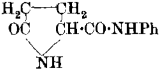
The *ditartrate* was obtained by adding freshly prepared, finely powdered silver tartrate to a hot solution of the di-iodide; after boiling for ½ hour, the solution was filtered and concentrated. The concentrated aqueous solution of the tartrate, however, would not crystallise, but remained as a thick syrup. The latter was therefore taken up in a little water and fractionally precipitated with alcohol; this precipitation was repeated twice and the final syrup redissolved in water and converted into dibromide. The latter, however, was inactive.

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, March 24th, 1928.*]

CLXV.—*The Action of Aniline on* d-*Glutamic Acid.*

By WILLIAM HERBERT GRAY.

IT has been stated by Abderhalden and Schwab (*Z. physiol. Chem.*, 1926, **153**, 88) that a new acid, 2-hydroxypyrroline-5-carboxylic acid (I), is formed when *d*-glutamic acid is heated with aniline, and

(I.)   (II.)

that this, unlike 2-pyrrolidone-5-carboxylic acid, of which it is th enolic form, can be reduced to 2-hydroxypyrrolidine-5-carboxyli acid. Working under the conditions described by these authors the writer has indeed obtained a substance with the same meltin point, and giving the same colour reactions, as attributed by then to 2-hydroxypyrroline-5-carboxylic acid, but this proves to be th anilide of a dehydrated glutamic acid. From the following con siderations this dehydrated acid is not the acid (I): on treatment o the anilide with two atoms of bromine, one atom only is taken up with formation of the corresponding *p*-bromoaniline derivative it gives a monoacetyl compound when boiled with a large excess acetic anhydride; and it is not reduced by hydrogen, with platinu catalyst, under a pressure of two atmospheres. The anilide mus have, therefore, the alternative structure (II). It is dextrorotator but is found to be the anilide of *l*-2-pyrrolidone-5-carboxylic aci the same product being obtained by heating this acid with anilin The racemic anilide is formed to a small extent when glutamic aci is heated with aniline for a comparatively long time. It is much le soluble than the anilide of the *l*-form, so that its absence from t product obtained in the first case indicates that racemisation is slo compared with ring-closure and anilide formation, and this view borne out by the fact that the *dl*-anilide is rapidly formed fro *dl*-2-pyrrolidone-5-carboxylic acid under the same conditions.

Abderhalden and Schwab state that their hydroxypyrrolin carboxylic acid gives positive Millon and xanthoprotein tests, a is particularly distinguished from the ketonic form by developing yellow coloration with *p*-dimethylaminobenzaldehyde. The anili is found to give all these reactions, and 2-pyrrolidone-5-carboxy acid gives the yellow coloration if a trace of aniline is introduce In a later paper (Abderhalden and Schwab, *Z. physiol. Che* **1926**, **157**, 196) it is mentioned that the same product is obtain when glutamic acid is heated with diphenylamine. On repeati this experiment, the product obtained by the author had in eve

instance the properties of a 2-pyrrolidone-5-carboxylic acid. Attempts to reduce the substance so prepared were made, in order to be certain that it was not actually the enolic form, possibly indistinguishable from pyrrolidonecarboxylic acid by the other tests applied. In these attempts, hydrogen under a pressure of two atmospheres was used, and either Willstätter's platinum-black as modified by Feulgen (*Ber.*, 1921, **54**, 360), the very active platinum oxide–ferrous salt catalyst of Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 1397), or palladinised barium sulphate, the activity of these being verified in every case by control reduction of quinine or salicylaldehyde, but in no case was hydrogen absorbed. This is additional evidence of the identity of the diphenylamine-treated product with 2-pyrrolidone-5-carboxylic acid, in which, as in other 2-pyrrolidone derivatives, the carbonyl group is resistant to reduction (compare Tafel and Stern, *Ber.*, 1900, **33**, 2226; McCay and Schmidt, *J. Amer. Chem. Soc.*, 1926, **48**, 1933; Ramart-Lucas and Fasal, *Compt. rend.*, 1927, **184**, 1253; and Darapsky, *J. pr. Chem.*, 1927, **116**, 129).

The previous work of Hugounenc, Florence, and Couture (*Bull. Soc. Chim. biol.*, 1924, **6**, 672) appears to have been overlooked. These authors heated *d*-glutamic acid with aniline and obtained a product having practically the same melting point as that found by Abderhalden and Schwab. They correctly called this an anilide but, incorrectly, the anilide of glutamic acid.

EXPERIMENTAL.

1-2-*Pyrrolidone-5-carboxyanilide* (II).—A mixture of *d*-glutamic acid (43·5 g.) and aniline (217 c.c.) was heated under reflux at 205—210° for ½ hour, cooled, and filtered from a small undissolved residue. Ether (130 c.c.) was then added, and the crystalline solid which separated was washed with ether and dried (20·8 g., m. p. 187°). The filtrate was concentrated and treated with ether, giving a further ·8 g. After one recrystallisation from methyl alcohol the *anilide* was obtained pure, m. p. 191°, $[\alpha]_D^{15°} + 17·9°$ in 80% alcohol ($c =$ ·8). The foregoing procedure is that of Abderhalden and Schwab; better yield and a cleaner product are obtained by heating the mixture at 150° instead of 210° and treating the product with acetone in place of ether. Water or ethyl alcohol is equally effective for recrystallisation; the anilide separates from the latter in well-formed, flat tablets with pointed ends, exhibiting a considerable twinning tendency. It is readily soluble in cold glacial acetic acid, chloroethyl alcohol, or concentrated hydrochloric acid, moderately easily soluble in methyl and ethyl alcohol, sparingly in cold water but more readily on heating (1 in 7·4), and almost insoluble in benzene (Found: C, 64·7; H, 6·0; N, 13·5. $C_{11}H_{12}O_2N_2$ requires

C, 64·7; H, 5·9; N, 13·7%). On hydrolysis by boiling dilute sodium hydroxide solution it yielded aniline and *d*-glutamic acid.

Preparation from 1-2-*pyrrolidone*-5-*carboxylic acid*. This acid prepared by the method of Menozzi and Appiani (*Gazzetta*, 1894 **24**, 373), is advantageously purified by extraction with acetone, in which the *dl*-acid is very sparingly soluble, and recrystallisation o the acetone-soluble material from alcohol. For preparation of th anilide, the acid was heated at 150° with five parts of aniline fo 6 hours. On removal of a portion of the excess of aniline in a vacuum the anilide crystallised. It had the same melting point and rotatio as that described above.

1-2-*Pyrrolidone*-5-*carboxy*-p-*bromoanilide*.—*l*-Pyrrolidonecarboxy anilide (1 g.), dissolved in 50% aqueous acetone (15 c.c.), was treate with bromine water (2 at. Br). This was immediately decolorise and colourless needles separated (1·2 g.), m. p. 212°; these crysta lised from alcohol in large prisms (Found: Br, 28·2. $C_{11}H_{11}O_2N_2$B requires Br, 28·2%). The substance is insoluble in cold conce trated hydrochloric acid. On hydrolysis, it yielded *p*-bromoanilin

1-*Acetyl*-2-*pyrrolidone*-5-*carboxyanilide*.—The anilide (5 g.) w boiled with acetic anhydride (25 c.c.; 11 mols.) for 1½ hours, t excess of anhydride removed by distillation, and the oil treat with ether (30 c.c.). A small quantity of solid which separated w rejected, and a solution of the remainder in alcohol was treated wi water until turbid; colourless needles then separated (1·2 g.) whic after recrystallisation from boiling water, had m. p. 166° (Foun C, 63·2; H, 5·5; N, 11·4. $C_{13}H_{14}O_3N_2$ requires C, 63·4; H, 5 N, 11·4%).

1-*Dibenzyl*-2-*pyrrolidone*-5-*carboxyanilide*.—*l*-Pyrrolidonecarbo anilide (5·5 g.), benzyl chloride (14·7 c.c.), and powdered sodi hydroxide (1·7 g.) were mixed, treated with a drop of pyridine, a heated for 7 hours at 100°. The acidified reaction-mixture yiel to ether 1·1 g. of crystalline material, which separated from lig in fern-like crystals, or from aqueous acetone in large, colour plates, m. p. 158°. It was insoluble in water, sparingly soluble ligroin, and readily in acetone (Found: C, 78·1; H, 6·25; N, $C_{25}H_{24}O_2N_2$ requires C, 78·1; H, 6·3; N, 7·3%).

Attempted Reduction of 1-2-*Pyrrolidone*-5-*carboxyanilide*.— anilide (1 g.), dissolved in glacial acetic acid (30 c.c.), with addi of active platinum oxide (0·01 g.), and ferric chloride solut (0·11 c.c containing 0·0007 g.), were shaken with hydrogen und pressure of 2 atmospheres for 27 hours. No hydrogen was absor and the original substance was recovered unchanged.

dl-2-*Pyrrolidone*-5-*carboxyanilide*.—*dl*-2-Pyrrolidone-5-carbox acid (4 g.), prepared by the method of Haitinger (*Monatsh.*, 188

228), was heated with aniline (20 c.c.) under reflux at 205—210° for ½ hour. When cool, the solid product was washed with ether, leaving undissolved 4·1 g. of a colourless solid, *m. p.* 204°, unchanged by recrystallisation from water, the *anilide* then forming elongated, striated plates. It is considerably less soluble than the *d*-form (1 in 24, approximately, in water at 100°) and is almost insoluble in ethyl alcohol or aqueous acetone. β-Chloroethyl alcohol dissolves it fairly readily (Found: C, 64·45; H, 5·9. $C_{11}H_{12}O_2N_2$ requires C, 64·7; H, 5·9%).

Heating d-*Glutamic Acid with Diphenylamine.*—A mixture of *d*-glutamic acid (18·6 g.) and diphenylamine (93 g.) was heated at 205—210° for ½ hour. The dark-coloured product was extracted with boiling ether, leaving 14·2 g. undissolved. 3 G. of this were extracted with cold water, and the insoluble tar was rejected. The almost colourless remainder gave, on recrystallisation from alcohol, 0·8 g., m. p. 186° (Found: C, 46·6; H, 5·7. $C_5H_7O_3N$ requires C, 46·5; H, 5·5%). The same substance was obtained by recrystallising the crude product from methyl alcohol. It does not decolorise bromine or permanganate solution appreciably. Bromine is dissolved by an aqueous solution of the substance to a considerably greater extent than by water, but is removed entirely in a vacuum, leaving the original substance, m. p. 188° (Found: C, 46·2; H, 5·4. Calc.: C, 46·5; H, 5·5%). For the attempted hydrogenation by the catalysts mentioned on p. 1265, glacial acetic acid, water, or alcohol was used as solvent. From the mother-liquor of the above substance a small quantity of *l*-pyrrolidonecarboxylic acid, m. p. 160°, $[\alpha]_D^{15°}$ −10·36° in water, was isolated.

As it is stated in general terms by Abderhalden and Schwab (*Z. physiol. Chem.*, 1926, **157**, 196) that the time of heating has an influence on the nature of the product, the preceding preparation was repeated, heating at the same temperature being prolonged to 2½ hours. The same product was obtained. The effect of higher and lower reaction-temperatures was tried; at 240°, only tarry products, and at 155—165° a higher proportion of *l*-pyrrolidonecarboxylic acid, were obtained.

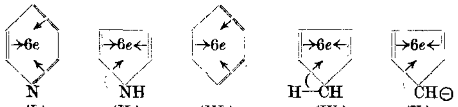
The author desires to express his warmest thanks to Dr. T. A. Henry for his kind interest and valuable advice, and to Mr. A. Davies for assistance in the preparation and analysis of the products described.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON. [*Received, February 28th,* 1928.]

CLXVI.—*The Tautomerism of* cyclo*Pentadienes. Part I. Some Derivatives of Methyl*cyclo*pentadiene.*

By Frank Robert Goss and Christopher Kelk Ingold.

The *theory that aromatic systems owe their stability to a sextuple* valency group is expressed in one form by the centric structure, and in another by Thiele's partial-valency formula, for benzene, and these may be regarded as the classical representatives of the two views that the association is central and peripheral respectively. The principal evidence in favour of the general conception is, however, that given by Bamberger (*Ber.*, 1891, **24**, 1758; 1893, **26**, 1946; *Annalen*, 1893, **273**, 373), whose arguments are simple and conclusive: pyrroles are exceptionally weak bases, and this is because the salt-forming valencies of the nitrogen atom (in modern terminology, its unshared electrons) are required to form the sextuple group; pyridines, on the other hand, are relatively strong bases, because the sextuple group can be formed without calling on the latent valencies of the nitrogen atom, which therefore remain available for salt-formation. Without assumption as to the precise location of the stable group, the conception may be expressed by (I) and (II), where each arrow denotes a contributing duplet. An interesting application has been made by Armit and Robinson (J., 1925, **127**, 1605), who have shown that the existence of the stable group is consistent with the properties of anhydronium bases, and yet another illustration forms the subject of this paper.

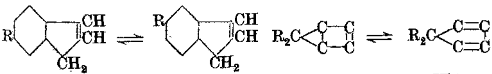


(I.) (II.) (III.) (IV.) (V.)

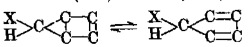
In a recent communication (Baker, Cooper and Ingold, this vol., p. 426), a valency-group of a different type was considered, and it was shown that the non-basicity of nitriles and the power of acetylenes to yield metallic derivatives are phenomena of identical origin. Excluding the triarylmethyls, which require separate discussion (see this vol., p. 905, footnote), the only other group of hydrocarbons characterised by their ability to form highly stable metallic compounds are the *cyclo*pentadienes, including their polynuclear derivatives, indene and fluorene. It will be evident that the reasoning by which the properties of acetylenes were correlated with those of nitriles also enables the chemistry of the

above-mentioned cyclic hydrocarbons to be correlated with that of the very weak bases considered by Bamberger. Benzene (III) is obviously in the same case as pyridine in regard to its ability to provide the electrons for the stable sextet, but *cyclo*pentadiene can do so only by the appropriation of the electrons of one of its hydrogen atoms: it is this circumstance which gives to the hydrocarbon and its derivatives properties analogous to those of an acid (IV), and confers stability on the corresponding anion (V).

The same circumstance should also confer tautomeric (prototropic) mobility on *cyclo*pentadiene and indene, but probably not on fluorene, since the lateral rings will tend to fix the structure of the central ring in this hydrocarbon. The case of indene has already been examined by Ingold and Piggott (J., 1923, **123**, 1469), who found that it exhibited prototropy; derivatives of types (VI) and (VII) were identical and they also responded to the "fission" and "substitution" tests (*loc. cit.*) for tautomeric mobility in symmetrical systems. This series of papers has originated in an attempt to test the matter for the simple *cyclo*pentadiene nucleus. Many simple *cyclo*pentadienes have been studied by Perkin, Thorpe, Farmer, Seeley, and others, who have shown that they exhibit valency-tautomerism of the intra-annular type; that is to say, they are not only *cyclo*pentadienes, but also *dicyclo*pentenes (VIII, IX). These compounds, however, were unsuitable for our purpose, since they contain the *gem*-grouping indicated in the formulæ (or an equivalent spiran ring), and thus do not contain a hydrogen atom which might be induced to ionise by the tendency to form a nuclear electron-group. We have therefore undertaken the study of analogous compounds (X, XI) which do not suffer from the disability mentioned, and in this paper derivatives are described in which the *gem*-dialkyl group of the previous work is replaced (i) by $^{CH_3}_{H}{>}C$, and (ii) by $^{CO_2Me}_{H}{>}C$ and $^{CO_2Et}_{H}{>}C$. It may be stated here that the results obtained, although, perhaps, not wholly conclusive, tend strongly in the direction indicated above.

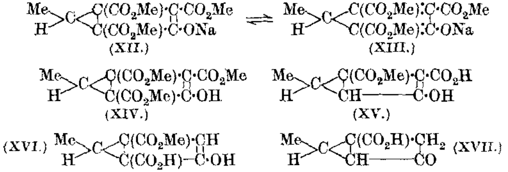


(VI.) (VII.) (VIII.) (IX.)

(X.)  (XI.)

For the preparation of the first series of compounds we employed the method whereby Perkin and Thorpe originally synthesised the

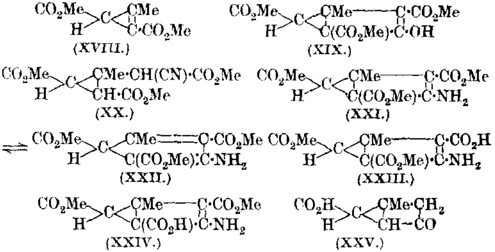
sodio-derivative of ethyl 5 : 5-dimethyl*cyclo*pentadien-3-ol-1 : 2 : 4-tricarboxylate (dimethyl*dicyclo*pentenoltricarboxylate) from ethyl αα′-dibromo-ββ-dimethylglutarate, ethyl sodiomalonate, and sodium ethoxide. Using ethyl dibromo-β-methylglutarate, we obtained the corresponding yellow sodium compound of the 5-methyl-5-hydrogen series, which resembled its analogue, but was unfortunately much more soluble and hence difficult to isolate and purify. This obstacle was, however, largely overcome by the use of methyl in place of ethyl esters, and it is therefore the yellow sodium compound (XII, XIII) which has been examined in the greatest detail. Its hydrolysis was followed through the stages represented, as to one tautomeric form, by (XIV) and (XV or XVI), the final product being (XVII).



(XII.) (XIII.) (XIV.) (XV.) (XVI.) (XVII.)

The starting point of the second series of preparations was the methyl*cyclo*propenedicarboxylic ester (XVIII), the constitution of which rests on results described in several former communications (Goss, Ingold, and Thorpe, J., 1923, **123**, 327, 3342; 1924, **125**, 1927; 1925, **127**, 460), in which it is shown, *inter alia*, that the additive reactions of the corresponding acid definitely determine that the double linking is in the position indicated, and not in the symmetrical endocyclic position or the semicyclic position. By the interaction of this ester with methyl sodiomalonate and sodium methoxide, the compound (XIX) might obviously be produced, and there is evidence that this is the case, although extensive side reactions also occur which render difficult the purification of the dicyclic product. The condensation of the *cyclo*propene ester with methyl sodiocyanoacetate, however, pursues a smoother course and a *cyclo*propane-cyanoacetic ester (XX) is formed, which on ring-closure produces an amino-ester, apparently analogous to the hydroxy-esters which are formed when the corresponding *cyclo*propane-malonic esters undergo ring formation. The amino-compound is a weak base, and it also behaves as a weak acid, since a solid sodio-derivative is obtainable. By analogy with the hydroxy-esters it may be represented by (XXI) and (XXII), possibly together

with the corresponding imino-phases. Partial hydrolysis to a compound represented, as to one phase, by (XXIII) or (XXIV) can be effected without loss of the amino-group, and the final hydrolysis product is the nitrogen-free acid (XXV). Closely similar results were obtained when the ethyl ester corresponding to (XVIII) was used, the final product being the same acid (XXV).

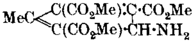


(XVIII.) (XIX.) (XX.) (XXI.) (XXII.) (XXIII.) (XXIV.) (XXV.)

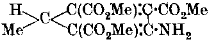
This acid is identical with that represented by formula (XVII). Intra-annular tautomerism is insufficient to account for this result, and it follows that in either or both the series examined nuclear prototropy must be present.

In following up the matter we were necessarily bound by practical considerations, but are able to include in this paper an account of a detailed study of the mild oxidation of the amino-ester (XXI, XXII). Of the six products isolated and recognised, the most significant from the structural point of view are β-methylglutaconic acid, β-acetylacrylic acid and α-methylglutaconic acid. The production of β-methylglutaconic acid may be regarded as normal, since it corresponds to the isolation of αα-dialkyl aconitic acid derivatives by oxidative degradation of 5 : 5-dialkyl*cyclo*pentadiene compounds. β-Acetylacrylic acid, however, is a substance which would have been expected to arise more readily from compounds of the series prepared from β-methylglutaric acid, and we suggest that the form (XXVI) is an intermediate in its production. The formation of α-methylglutaconic acid is difficult to explain in any complete way, but the most probable view seems to be that it is produced through form (XXVII), or a valency tautomeride. The formation of the tautomeric modifications (XXVI) and (XXVII) from (XXI) or (XXII) involves a mobile-hydrogen change of precisely the type required to effect the conversion of an acid of formula (XVII) into its isomeride (XXV), and *vice versa*. At this

stage in the research our stock of material, which had taken long to accumulate, became exhausted, but the work is being continued and it is hoped later to obtain further evidence regarding the structural and other conditions required to produce the nuclear transformations, the existence of which has been indicated.



(XXVI.)



(XXVII.)

EXPERIMENTAL.

(A) *Syntheses starting from β-Methylglutaric Acid.*

*Methyl 5-Methyl*dicyclo*penten-3-ol-1:2:4-tricarboxylate* (*Methyl 5-Methyl*cyclo*pentadien-3-ol-1:2:4-tricarboxylate*) (XIV).—Methyl malonate (16 g.) and methyl dibromo-β-methylglutarate (Ingold, J., 1922, **121**, 2685) (20 g.) were successively added to a solution of sodium methoxide prepared from sodium (5 g.) and methyl alcohol (60 g.). After being kept at the ordinary temperature for 15 hours, the mixture was heated just below the boiling point for 3 hours, cooled, poured on 50 g. of ice, and evaporated at room temperature until separation of the sodium compound was complete. The solid was collected (12 g.) and crystallised from methyl alcohol. *Methyl sodio-5-methyl*dicyclo*penten-3-ol-1:2:4-tricarboxylate* (XII, XIII) separated in bright yellow needles, m. p. 270° (decomp.), which gave a deep violet colour with ferric chloride (Found: Na, 8·0. $C_{12}H_{13}O_7Na$ requires Na, 7·9%). For the preparation of the free *hydroxy-ester*, the sodium compound was covered with ether and shaken with dilute hydrochloric acid until the yellow colour disappeared. The colourless oil obtained when the ethereal extract was dried and evaporated had b. p. 180°/1 mm. (Found: C, 53·6; H, 5·1. $C_{12}H_{14}O_7$ requires C, 53·3; H, 5·2%).

*Ethyl 5-Methyl*dicyclo*penten-3-ol-1:2:4-tricarboxylate* (*Ethyl 5-Methyl*cyclo*pentadien-3-ol-1:2:4-tricarboxylate*).—This was prepared in a similar manner from ethyl malonate, ethyl dibromo-β-methylglutarate (Ingold, *loc. cit.*), and ethyl-alcoholic sodium ethoxide, with the exception that, after being kept over-night in the cold, the mixture was heated just short of the b. p. for 24 hours. The mixture was poured into water and extracted twice with ether; the aqueous solution was then saturated with carbon dioxide and thoroughly extracted with much ether. The second extract on evaporation yielded a residue which, after drying in a desiccator, set to a yellow solid, m. p. about 70°; this contained sodium and gave a violet colour with ferric chloride. The free *hydroxy-ester*, which was obtained as in the preceding example, behaved similarly

towards ferric chloride (Found: C, 57·2; H, 6·1. $C_{15}H_{20}O_7$ requires C, 57·7; H, 6·5%).

*Methyl Hydrogen 5-Methyl*dicyclo*penten-3-ol-*1 : 2(or 1 : 4)-*dicarboxylate* (*Methyl*cyclo*pentadienoldicarboxylate*) (XV or XVI).—The sodio-methyl ester was digested at the ordinary temperature for 72 hours with 30% methyl-alcoholic potassium hydroxide. During this period the sodio-compound dissolved, and a yellow precipitate, consisting of *dimethyl potassium potassio-5-methyl*dicyclo*pentenoltricarboxylate* (Found: K, 23·1. $C_{11}H_{10}O_7K_2$ requires K, 23·5%), appeared, which was collected and washed with methyl alcohol. On decomposing this with acid and extracting the solution with ether the *methyl hydrogen* ester was obtained as a viscous liquid which gave a deep violet colour with ferric chloride (Found: C, 54·1; H, 5·4. $C_9H_{10}O_5$ requires C, 54·5; H, 5·1%).

Ethylation of the Yellow Methyl Sodio-compound (XII, XIII).—The sodio-compound was boiled with an excess of ethyl iodide in ethyl-alcoholic solution for 24 hours. The excess of alcohol was removed by evaporation, and the residue poured into water and extracted with ether. The extract was washed with much water, dried, and distilled; *methyl 5-methyl-*2(or 4)-*ethyl*dicyclo*pentan* (or cyclo*penten*)-3-*one*-1 : 2 : 4-*tricarboxylate* was then obtained as a colourless neutral oil, b. p. 210°/6 mm. (Found: C, 56·2; H, 6·1. $C_{14}H_{18}O_7$ requires C, 56·3; H, 6·1%).

5-*Methyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (5-*Methyl*cyclo*penten*-3-*one*-1-*carboxylic Acid*) (XVII, XXV).—This acid was obtained when any of the above ring compounds (except the ethylation product) was boiled for 2 hours with hydrochloric acid. The cooled solution was extracted with much ether, and the residue obtained on evaporation of the extract crystallised from ligroin (b. p. 80—100°), needle clusters being obtained, m. p. 60° (Found: C, 59·9; H, 5·7. $C_7H_8O_3$ requires C, 60·0; H, 5·8%). The acid gives no colour with ferric chloride, and on oxidation with alkaline permanganate yields only oxalic acid. The *oxime*, which was prepared by using the theoretical quantity of hydroxylamine hydrochloride and one equivalent of sodium carbonate, crystallised when the solution was warmed for a few minutes, and separated from ethyl acetate in needles, m. p. 216° (decomp.) (Found: C, 53·8; H, 5·7. $C_7H_9O_3N$ requires C, 54·2; H, 5·9%).

(B) *Syntheses starting from 3-Methyl-Δ^2-*cyclo*propene-*1 : 2-*dicarboxylic Acid.*

*Methyl 3-Methyl-*1 : 2-*dicarbomethoxy*cyclo*propane-3-cyanoacetate* (XX).—Methyl 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylate (Goss, Ingold, and Thorpe, *loc. cit.*) was added to a methyl-alcoholic solu-

tion containing one equivalent of methyl sodiocyanoacetate. The mixture was kept for 2 hours at the ordinary temperature, then boiled for 2 hours, cooled, and poured into water. The oil was extracted with ether, and the extract was washed well with water, and once with dilute sodium hydrogen carbonate solution, dried, and evaporated. The residue on distillation yielded a series of volatile fractions consisting of the original *cyclo*propene ester and its methyl alcohol addition-product (*loc. cit.*), together with the *cyano-ester* (XX), b. p. 200°/20 mm. (Found: C, 54·1; H, 5·2. $C_{12}H_{15}O_6N$ requires C, 53·5; H, 5·6%). The yield (15%) could not be increased by prolonging the period of the reaction, and hence probably represents the equilibrium attained by the Michael addition-reaction in the presence of the side-reaction leading to the methoxy-compound.

*Methyl 3-Amino-1-methyl*dicyclo*pentene-2 : 4 : 5-tricarboxylate* (*Methyl 3-Amino-1-methyl*cyclo*pentadiene-2 : 4 : 5-tricarboxylate*), *Forms A and B* (XXI, XXII).—A solution of the above cyano-ester in an excess of methyl-alcoholic sodium methoxide was kept over-night at the ordinary temperature, then heated just below the b. p. for 4 hours, cooled, and poured into water. The ethereal extract of the solution yielded on evaporation a small residue from which the *amino-ester B*, m. p. 186° (decomp.), was obtained by crystallisation from benzene or ether (Found: C, 53·5; H, 5·5. $C_{12}H_{15}O_6N$ requires C, 53·5; H, 5·6%). This compound is somewhat soluble in cold alkali and readily soluble in hydrochloric acid; on keeping, it becomes converted into the more stable isomeride-A mentioned below, which is present along with B in the residue from the ethereal extract. The aqueous solution remaining from the ether extraction was saturated with carbon dioxide and again extracted with ether. This extract yielded the *amino-ester A*, m. p. 130° (decomp.), which was finally purified by crystallisation from ligroin (Found: C, 53·9; H, 5·8; N, 5·7. $C_{12}H_{15}O_6N$ requires C, 53·6; H, 5·6; N, 5·2%). This isomeride is fairly readily soluble in caustic alkali, and also in mineral acid; it gives a red precipitate with diazotised aniline. Neither isomeride gives any noticeable colour with ferric chloride. Accompanying the A-compound in the residue from the second extract is a small quantity of a by-product, which has m. p. 186° and is not identical with B. We have not yet obtained sufficient for a detailed investigation, but the product appears to be resistant to hydrolysis by hot hydrochloric acid, and we originally isolated it by destroying the A-compound by this means.

The same compounds, together with others mentioned below, were obtained by the following method. Methyl 3-methyl-Δ^2-

*cyclo*propene-1 : 2-dicarboxylate (10 g.) was added to a solution of methyl cyanoacetate (6 g.) in methyl-alcoholic sodium methoxide prepared from 3 g. of sodium and 35 g. of methyl alcohol. After being kept over-night at the ordinary temperature the mixture was heated to just below the b. p. for 8 hours, and when cool poured into water. A yellow precipitate appeared and almost immediately redissolved, and the solution was then extracted with ether, saturated with carbon dioxide, and again extracted, by which means the two isomeric amino-esters were isolated as described above. The aqueous solution remaining was acidified with hydrochloric acid and again extracted with ether. The solid residue obtained on evaporation of this extract, on crystallisation from ether, yielded three compounds which were isolated in the order named: (1) 3-methoxy-3-methyl*cyclo*propane-1 : 2-dicarboxylic acid (Goss, Ingold, and Thorpe, *loc. cit.*), (2) the monomethyl acid-ester of this acid (*loc. cit.*), and (3) dimethyl hydrogen 3-amino-1-methyl*dicyclo*-pentene-2 : 4 : 5-tricarboxylate (see below), the last two substances being obtained in small amount only. The yield of the main product, namely, amino-ester-A, was usually about 12%, and the substitution of potassium methoxide for sodium methoxide effected no substantial improvement.

*Dimethyl Hydrogen 3-Amino-1-methyl*dicyclo*pentene-2 : 4 : 5-tricarboxylate* (*3-Amino-1-methyl*cyclo*pentadiene-2 : 4 : 5-tricarboxylate*) (XXIII or XXIV).—The amino-ester-A was left at the ordinary temperature in contact with 3*N*-methyl-alcoholic potassium hydroxide for 24 hours, during which it dissolved and a yellow precipitate consisting of the *potassium potassio*-salt of the dimethyl hydrogen ester appeared. When the yellow, aqueous solution of this compound was acidified with hydrochloric acid, the free *acid-ester* was precipitated; this after crystallisation from ether had m. p. 226° (decomp.) (Found: C, 51·7; H, 4·7; *M*, 255. $C_{11}H_{13}O_6N$ requires C, 51·7; H, 5·1%; *M*, 255). On working up the alcoholic mother-liquors, a further quantity of the same substance was obtained, together with an unidentified product, m. p. 97°, and some unchanged amino-ester-A. The dimethyl hydrogen ester gives an intense purple colour with ferric chloride, as also does its yellow potassium salt.

*1-Methyl*dicyclo*pentan-3-one-5-carboxylic Acid* (*1-Methyl*cyclo*penten-3-one-5-carboxylic Acid*) (XVII, XXV).—The amino-ester-A was boiled for 1 hour with hydrochloric acid, and the cooled and filtered solution extracted 20 times with ether. The solid residue, after crystallisation from ligroin, had m. p. 60° and was identical with the acid described on p. 1273.

Oxidation of the Amino-ester-A.—The use of alkaline permanganate and chromium trioxide in acetic acid, and sodium chlorate

and osmium tetroxide yielded oxalic acid as the only recognisable product, and potassium ferricyanide in the presence of potassium carbonate gave an intractable gum.

The amino-ester (2 g.) was digested with a solution of potassium persulphate (30 g.) and silver oxide (0·25 g.) in 25 c.c. of 2*N*-sulphuric acid, and the mixture was kept with frequent shaking at a temperature varying from 20° to 40° for some weeks. Several experiments were commenced simultaneously, and the products were worked up at intervals by extracting the solution with ether, washing the extract with sodium carbonate, acidifying the alkaline solution, and re-extracting the acid products. These were then boiled with 20% hydrochloric acid to complete the hydrolysis, and the solution was either evaporated to dryness or extracted with ether. Oxalic acid was removed as the calcium salt from the acids thus obtained and the remainder of the acid product was drained from gum and crystallised from dilute alcohol. Oxalic acid was obtained in all cases, and the chief by-product was fumaric acid, which was identified by direct comparison and by conversion into methyl fumarate. In one experiment a small amount of a very soluble acid, which appeared to be maleic acid but could not be wholly purified, was also obtained.

The oxidation of the amino-ester (2 g.) with hydrogen peroxide (50 c.c. of 6%) and ferrous sulphate (0·25 g.) was carried out in a similar way, excepting that the mixtures were shaken continuously at the ordinary temperature for periods of from 20 to 120 hours. Oxalic acid was formed in all cases, but in much smaller amount than in the previous series of experiments. The remaining acids were drained on porous porcelain, triturated with ether–ligroin, and crystallised from concentrated hydrochloric acid, an acid, m. p. 141—143°, identified by direct comparison as α-methylglutaconic acid (Found: C, 49·9; H, 5·5. Calc.: C, 50·0; H, 5·6%), being obtained. The hydrochloric acid mother-liquors on evaporation gave a stiff gum; this partly solidified and on draining yielded a product which, after crystallisation from ethyl acetate–ligroin, had m. p. 113—115° and was identified as the more fusible form of β-methylglutaconic acid (Found: C, 49·9; H, 5·5%). Extraction of the porcelain on which the original mixed acids had been drained, and combination of the product with the residues from the ether–ligroin solution, gave a dark brown gum in which, after some days, long needles appeared. After some crystals for inoculation had been collected, the whole product was repeatedly digested with charcoal in aqueous alcohol, and the acids were isolated again and seeded. Crystallisation occurred rapidly, and the drained product was crystallised twice from ether–ligroin, from which almost colourless needles, m. p. 125—126°, were obtained. The m. p. and analysis

(Found: C, 52·3; H, 5·7%) indicating β-acetylacrylic acid, a specimen of this substance was prepared by the recorded method and the identity confirmed.

Ethyl 3-*Amino*-1-*methyl*dicyclo*pentane*-2 : 4 : 5-*tricarboxylate* (-cyclo*pentadienetricarboxylate*).—A solution of ethyl methyl*cyclo*propenedicarboxylate (10 g.) and ethyl cyanoacetate (6·5 g.) in sodium ethoxide prepared from sodium (3 g.) and ethyl alcohol (36 g.) was kept over-night at the ordinary temperature, heated short of the b. p. for 6 hours, boiled for 2 hours, cooled, and poured into water. The *sodio*-derivative of the amino-ester, which was precipitated as a yellow solid contaminated with oil, was collected and washed well with ether (Found: Na, 7·1. $C_{15}H_{20}O_6NNa$ requires Na, 6·9%). The derivative is slightly soluble in water, but its yellow solution does not give a coloration with ferric chloride. Treatment with carbon dioxide decolorises the solution and produces an immediate precipitation of the *amino-ester*, which separates from ligroin in needles, m. p. 107° (Found: C, 57·5; H, 7·0. $C_{15}H_{21}O_6N$ requires C, 57·8; H, 6·8%). The compound is a weak base, for it may be precipitated from its solution in acids by large dilution; it is also a weak acid, because the addition of aqueous sodium hydroxide to its solution in alcohol precipitates the yellow sodium derivative which, as indicated above, is decomposed completely by carbonic acid. Only about half the total quantity of amino-ester formed (about 14%) is isolated by the method described above, and the remainder may be obtained as follows. The filtrate from the sodium compound was extracted with ether and saturated with carbon dioxide. The ethereal extract yielded the amino-ester, and a precipitate in the aqueous suspension consisted of the same substance. The filtrate from this yielded no further product when again extracted with ether, and was therefore acidified with hydrochloric acid. The ethereal extract from this solution yielded a gum which on keeping partly crystallised. The drained crystals, on crystallisation from xylene, yielded the *diethyl hydrogen amino-ester*, m. p. 199° (decomp.) (Found: C, 54·6; H, 5·9. $C_{13}H_{17}O_6N$ requires C, 55·1; H, 6·1%). Yield, about 1%.

Methylation of the Amino-ester.—The yellow sodium compound (0·5 g.) was boiled for 24 hours with a solution of methyl iodide (0·5 g.) in ethyl alcohol (6 c.c.). The *product*, isolated by extraction with ether after the mixture had been poured into water, readily solidified, and separated from ligroin in needles, m. p. 113° (Found: C, 58·8; H, 6·5. $C_{16}H_{23}O_6N$ requires C, 59·1; H, 7·1%).

Ethylation of the Amino-ester.—Ethylation was effected by the same method, and also by using the amino-ester, sodium ethoxide, and ethyl iodide. The *product* crystallised from ligroin in needles,

m. p. 118° (Found: C, 60·4; H, 7·7. $C_{17}H_{25}O_6N$ requires C, 60·6; H, 7·4%). These alkylation products were prepared in the hope that their oxidation would yield useful information, but experiments in this direction have so far not met with success.

Hydrolysis of the Amino-ester.—This experiment was carried out like that described on p. 1275, and with identical results.

We wish to thank the Chemical and Royal Societies for generous grants in aid of this work.

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CLXVII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXVI. The Nitration of ω-Chloro- and ω-Bromo-*p*-xylene.*

By CHRISTOPHER KELK INGOLD and EUGENE ROTHSTEIN.

ACCORDING to Holleman (*Rec. trav. chim.*, 1914, **33**, 1) toluene and its ω-chloro-derivatives yield the following proportions of *m*-derivative on nitration under corresponding conditions: $Ph{\cdot}CH_3$, 4·4%; $Ph{\cdot}CH_2Cl$, 4·2%; $Ph{\cdot}CHCl_2$, 33·8%; $Ph{\cdot}CCl_3$, 64·5%; and from these results it has been inferred that the successive replacement of the ω-hydrogen atoms in toluene by chlorine increases the electron-affinity and *m*-orienting tendency of the side chain. Nevertheless, the figure for benzyl chloride is anomalous from this point of view, and a reinvestigation of the nitration of this substance is being undertaken in these laboratories.* In the meantime, the development (Burton and Ingold, this vol., p. 904) of a hypothesis of orientation for conjugative additions required, for its application to the addition of halogens to hydrocarbons, a qualitative comparison of the orienting effects of $-CH_3$ on the one hand and $-CH_2Cl$ and $-CH_2Br$ on the other; for, in the absence of the necessary *direct* knowledge relating to anionotropy, the hypothesis may be applied by making use of the analogy (*loc. cit.*) between the *op*-orienting power of groups in aromatic substitution, and their action in facilitating anionotropic change. For this reason we have examined the nitration of ω-chloro- and ω-bromo-*p*-xylene, and are able to show that predominating substitution occurs in the position ortho to the methyl group. These experiments complete the evidence on the basis of which Burton and Ingold explained the course pursued by the action of bromine on butadiene and isoprene,

* This has since been completed by Miss F. R. Shaw, who finds that 16% of *m*-isomeride is produced.

and predicted the results which should accrue from a re-examination of earlier work on the addition of bromine to βγ-dimethylbutadiene.

EXPERIMENTAL.

ω-Bromo-*p*-xylene (60 g.) was converted into *p*-tolylcarbinyl acetate by heating for 1·5 hours under reflux with acetic acid (20 g.) and potassium acetate (30 g.), and the acetate (46 g.) hydrolysed with boiling 10% alcoholic sodium hydroxide (150 c.c.). The carbinol, after crystallisation from ligroin, was treated with a 20% excess of phosphorus trichloride, and the resulting ω-chloro-*p*-xylene (yield, 87%) purified by careful fractionation.

A solution of ω-chloro-*p*-xylene (16·1 g.) in acetic anhydride (30 c.c.) was added very gradually to a solution of fuming nitric acid (9 g.) in acetic anhydride (20 c.c.) at 10—12°. After 6 hours, ice was added, and, after the decomposition of the excess of acetic anhydride, the product was neutralised with sodium carbonate and extracted with ether. It contained a considerable quantity of un-nitrated ω-chloro-*p*-xylene (which in itself guarantees the absence of dinitro-derivatives), but before this was removed by distillation, 6·3 g. of practically pure ω(1)-chloro-3-nitro-*p*-xylene separated and was collected. The mononitration product had b. p. about 140°/4 mm., and the distillate (8·6 g.) yielded a further 4·6 g. of the same chloronitro-compound. The liquid portion, on treatment with ethyl-alcoholic trimethylamine, precipitation of the quaternary ammonium chlorides with ether, and conversion of these into the picrates (3·0 g.), gave 3-nitro-4-methylbenzyltrimethylammonium picrate (this vol., p. 1217), together with an isomeride which could not be separated (Found, for a mixture having m. p. 125—128°: C, 46·6; H, 4·6. Calc.: C, 46·7; H, 4·3%). The ethereal alcoholic filtrate from the quaternary chlorides on evaporation yielded a halogen-free liquid, b. p. 115—120°/3 mm. (1·7 g.), consisting essentially of 2- and 3-*nitro*-4-*methylbenzyl ethyl ethers* (Found: C, 62·1; H, 7·1. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7%), and containing a considerable proportion of the 3-nitro-ether, as was proved by treatment with hydrogen bromide in acetic acid, ω(1)-bromo-3-nitro-*p*-xylene then being obtained. The proportion of nitration in position 3 is therefore more than 73%. The ω(1)-chloro-3-nitro-*p*-xylene was identified by direct comparison with the product described by Steven, Short, and Gladding (J., 1920, **117**, 525).

The nitration of ω-bromo-*p*-xylene and the separation of ω(1)-bromo-3-nitro-*p*-xylene (this vol., p. 1217) was carried out in a similar way, excepting that, owing to the tendency of the bromonitro-compound to decompose on distillation, the unchanged

ω-bromo-*p*-xylene was distilled from a water-bath at 3 mm. after each separation of the crystalline bromonitro-compound. The yield of the latter was 66% of the nitration product, and the remainder contained a further quantity, as was shown by conversion into a mixture of nitro-4-methylbenzyltrimethylammonium picrates, from which the 3-nitro-salt was separated. The small ultimate residues obtained after separation of the quaternary salt consisted as before of nitro-4-methylbenzyl ethyl ethers.

We wish to thank the Chemical Society for a grant in aid of this work.

THE UNIVERSITY, LEEDS. [*Received, April 2nd*, 1928.]

CLXVIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXVII. The Nitration of some Aromatic Phosphonium, Arsonium, and Stibonium Salts.*

By CHRISTOPHER KELK INGOLD, FLORENCE RUTH SHAW, and IAN STUART WILSON.

THIS paper records the results which have been obtained in the course of studies on the nitration of phenyltrimethyl-phosphonium, -arsonium, and -stibonium picrates and of benzyltrimethyl-phosphonium and -arsonium picrates. The proportions of *meta*-derivative are shown in the following table, in which the corresponding data for ammonium salts (Vorländer and Siebert, *Ber.*, 1919, **52**, 283; Goss, Hanhart, and Ingold, J., 1927, 250) are included for comparison.* It will be observed that there is a general decrease in the proportion of *m*-substitution in the direction of an increasing atomic number:

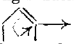
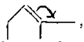
Cation.	$R\cdot\overset{+}{N}Me_3$.	$R\cdot\overset{+}{P}Me_3$.	$R\cdot\overset{+}{As}Me_3$.	$R\cdot\overset{+}{Sb}Me_3$.	
R = Phenyl	100·0	100·0	98·2	86·3	% *m*-substitution
R = Benzyl	88·0	10·1	3·4	—	,,

Ingold, Ingold, and Shaw (J., 1927, 813) discussed the influence of atomic number on the *m*-orienting effect of positive poles and suggested that, since the positive field emanates from the atomic nucleus, the envelopment of the latter by additional electron-

* Contemporaneously with these experiments, others on similar lines have been carried out by Dr. F. Challenger at Manchester, whose studies include the nitration of tribenzyl-phosphine and -arsine oxides and, together with those here described, constitute the first definite comparisons along the lines indicated.

shells in the larger atoms will diminish the field beyond the surface of the atom, and hence diminish *m*-orientation. The *m*-orienting sequence for compounds such as the above was predicted on this basis, and the results, which (excepting those for the ammonium compounds) were unknown at the time, justify the forecast. Pollard and Robinson subsequently suggested (J., 1927, 2772), as the determining circumstance, the principle that the greater the volume of the central charged atom, the greater should be the electrostriction of the organic cations by the anions in a nitration solution. This, however, does not appeal as an adequate cause, in view of Fajans' demonstration (*Naturwiss.*, 1923, **11**, 105) that the smaller a cation the more extensive *ceteris paribus* is the process of co-ordination, and its precursor, electrostriction, with a given anion. Whether we consider the direct influence of atomic size on the field, or the degree of electrostriction by anions, as the essential cause, a comparison of different cases requires the assumption of the approximate equivalence of centrally-acting charges. On various kinds of physical evidence relating to electrovalent compounds, departures from *strict* equivalence are to be expected, but in our view these are not to be regarded as significant in view of the magnitude of the differences under consideration. Chatterjee and Robinson's contention (J., 1927, 2781) that Ingold, Ingold, and Shaw's view is *invalidated* by this cause is entirely devoid of supporting evidence. There is one further consideration, namely, the effect of the stability of the -onium complexes themselves. The stability of an -onium complex may be deduced from the relative extents of the two simultaneous decompositions undergone by suitably constituted quaternary hydroxides, etc. (Hanhart and Ingold, J., 1927, 997), and we intend to institute a comparison between aromatic substitutions and exhaustive methylations on these lines.

Addendum by J. W. BAKER [*Received, April 23rd*, 1928].—The damping action of (1) external electron shells (this paper and cited references) and (2) an intercalated double linkage (Baker and Wilson, J., 1927, 843; Baker and Eccles, *ibid.*, p. 2125) on the meta-orienting action of a positive pole situated in the side chain of a benzene derivative has now been studied, and each condition is found to cause a considerable loss of meta-orienting power. In a recent paper Robinson and Zaki (J., 1927, 2485) stated that Baker and Wilson contested the *op*-directing influence of an ethenoid centre; but this is incorrect, since the investigation of the latter authors was concerned only with the relative amounts of *meta*-nitration produced *by the nitro-group* when the latter is separated from the benzene nucleus by an unsaturated carbon

chain, $CHPh{:}CH{\cdot}NO_2$, and by a saturated chain of equal length, $CH_2Ph{\cdot}CH_2{\cdot}NO_2$. This effect, if propagated by conjugated polarisation to the nucleus, should lead to more pronounced meta-substitution in the former case than in the latter. The reverse is true (2% and 13% respectively). Since, on nitration, *p*-nitrobenzylidenephenylnitromethane, $CPh(NO_2){:}CH{\cdot}C_6H_4{\cdot}NO_2$ (in which *the double bond is similarly situated with respect to the nucleus* but is no longer in the direct path of transmission from the nitro-group) yields 21% of meta-isomeride, it was inferred that the recognised *op*-directive influence of the vinyl double bond is not sufficiently strong completely to annul the meta-directing shift originating in the nitro-group when this effect is not transmitted to the nucleus through the ethenoid centre. These results confirmed the conclusion reached by Baker and Ingold (J., 1927, 832) and Cooper and Ingold (*ibid.*, p. 836) relating to the propagation of meta-directing influences from the side chain to the nucleus by the mechanism  instead of , a view substantiated by independent evidence by Le Fèvre and Turner (this vol., p. 245) and differing in no essential point from that adopted by Robinson and Zaki.

Discussing the meta-nitration of benzaldoxime and its N-methyl ether in sulphuric acid, Brady and Miller (this vol., p. 338) remark that *this is contrary to the suggestion* (Ingold, *Ann. Reports*, 1926, **23**, 131) that the introduction of unsaturated centres between a meta-orienting group and the nucleus causes a very rapid damping of the orienting effect. Baker and Ingold, however, showed that the meta-orienting power of C=O (C=N, etc.) is due to the permanently positively charged carbon atom $\overset{\delta+}{C}{=}\overset{\delta-}{O}$ just as in $\overset{+}{N}\overset{-}{O}_2$. In $-\overset{+}{CH{=}NRR'}$ the carbon, not the nitrogen, must be regarded as the effective meta-directing atom, and its positive charge is enhanced as compared with carbon in $-\overset{\delta+}{C}{=}\overset{\delta-}{N}R$ by distribution (*Ann. Reports*, 1927, **24**, 115) of the ionic charge of the pseudo-basic system of which it forms part. The work of Forsyth, Nimkar, and Pyman (J., 1926, 800) on amidine salts, $-\overset{+}{C(NH_2){=}NRR'}$, has already provided evidence illustrating this effect (*Ann. Reports*, 1926, **23**, 140).

EXPERIMENTAL.

Phenyldimethylphosphine has been prepared (Michaelis, *Annalen*, 1876, 181, 359) with the aid of zinc methyl. We find that it can

readily be prepared by the action of magnesium methyl iodide on phosphenyl chloride in an atmosphere of hydrogen. A solution of phosphenyl chloride (25 g.) in an equal volume of ether was added to the Grignard solution prepared from methyl iodide (39·7 g.) and magnesium (6·7 g.). After 2 hours, ice-water was added, and the tertiary phosphine, recovered from the ethereal layer, was distilled (yield, 35%). Treatment with methyl iodide yielded the methiodide; this on addition to saturated aqueous sodium picrate precipitated *phenyltrimethylphosphonium picrate,* which separated from water in yellow needles, m. p. 132—133° (Found: C, 47·2; H, 4·3. $C_{15}H_{16}O_7N_3P$ requires C, 47·1; H, 4·4%).

Benzyl chloride in excess was allowed to react with trimethylphosphine (Renshaw and Greenlaw, *J. Amer. Chem. Soc.*, 1920, 42, 1472; Renshaw and Bell, *ibid.*, 1921, **43**, 916), and the deliquescent phosphonium chloride was dissolved in water, extracted with ether to remove the excess of benzyl chloride, and converted into *benzyltrimethylphosphonium picrate* by precipitation with aqueous sodium picrate. The salt separated from water in flattened prisms, m. p. 173° (Found: C, 48·7; H, 4·8. $C_{16}H_{18}O_7N_3P$ requires C, 48·6; H, 4·6%).

Phenyldimethylarsine (Burrows and Turner, J., 1920, **117**, 1378) was prepared from dimethyliodoarsine (Roberts, Turner, and Bury, J., 1926, 144), and converted through the methiodide into the quaternary picrate (m. p. 145°; Steinkopf and Schwer, *Ber.*, 1921, **54**, 14), as in the previous examples.

Benzyldimethylarsine was prepared as described by Roberts, Turner, and Bury (*loc. cit.*), excepting that the Grignard reaction was conducted in an atmosphere of hydrogen, and the yield thus increased to 33%. The methiodide yielded *benzyltrimethylarsonium picrate,* which crystallised from water in yellow prisms, m. p. 175—176° (Found: As, 16·9. $C_{16}H_{18}O_7N_3As$ requires As, 17·1%).

Phenyldi-iodostibine was prepared by Schmidt's method (*Annalen*, 1920, **421**, 188) and converted into phenyldimethylstibine by treatment with the requisite amount of magnesium methyl iodide in an atmosphere of hydrogen. The tertiary base (b. p. 110—115°/17 mm.; Grüttner and Wiernik, *Ber.*, 1915, **48**, 1759) was converted into the methiodide and thence into *phenyltrimethylstibonium picrate,* which crystallised from water in needles, m. p. 153° (Found: C, 38·1; H, 3·3. $C_{15}H_{16}O_7N_3Sb$ requires C, 38·2; H, 3·4%).

The conditions used by Vorländer and Siebert (*loc. cit.*) for the nitration of phenyltrimethylammonium nitrate were found to be unsuitable for the corresponding phosphonium picrate, which was therefore nitrated at 60° (7 hours) with a mixture of equal volumes of fuming nitric and sulphuric acids. The product, m-*nitrophenyl-*

trimethylphosphonium picrate, which was for the most part precipitated on addition of ice, the small remainder being obtained by neutralising the filtrate with ammonia, evaporating it, and extracting it with ethyl acetate, consisted of a single substance, m. p. 166—167° (Found: C, 42·15; H, 3·5. $C_{15}H_{15}O_9N_4P$ requires C, 42·25; H, 3·55%), the residues containing no trace of any isomeride. Although we were unable to establish satisfactory conditions for the quantitative application of Francis and Hill's method of orientation, the constitution of the substance follows from analogy with the preparation of the corresponding ammonium and arsonium salts.

The nitration of benzyltrimethylphosphonium picrate occurs much more easily than that of its lower homologue and a low temperature is necessary. The salt (4·0 g.) was added (1 hour) with stirring to nitric acid (30 g., *d* 1·5) at − 17°, and a further hour was allowed for completion of the reaction; ice (60 g.) was then added, and ammonia passed in to neutralise the free acid. The precipitate was collected and washed, the residues obtained on evaporation of the mother-liquors to dryness were extracted with acetone, and the residue from this solvent was washed with water, and so forth, until complete separation from ammonium salts had been effected (yields, 96·5, 97·5%). By crystallisation from water, pure p-*nitrobenzyltrimethylphosphonium picrate* was isolated (yields, 70·1, 72·3%) as needles, m. p. 188—189° (Found: C, 43·9; H, 4·0. $C_{16}H_{17}O_9N_4P$ requires C, 43·6; H, 3·9%), and the proportion of *m*-derivative in the remainder (Found: C, 44·4, 44·3; H, 4·0, 4·1%) estimated as usual by reduction and bromine-titration (Found: meta, 9·5, 10·7% of the total nitration products). The identity of the *p*-compound was proved by oxidation to *p*-nitrobenzoic acid. o-*Nitrobenzyltrimethylphosphonium picrate* was prepared by allowing *o*-nitrobenzyl chloride to react with trimethylphosphine in ethereal solution, and converting the quaternary chloride into the picrate with sodium picrate. It separated from water in small needles, m. p. 152—153° (Found: C, 43·9; H, 4·1%). m-*Nitrobenzyltrimethylphosphonium picrate*, prepared similarly from *m*-nitrobenzyl chloride, formed small needles, m. p. 171—172° (Found: C, 43·4; H, 4·1%), and the *p*-salt obtained in the same manner was identical with the principal nitration product. These salts gave correct results on reduction and bromine-titration by Francis and Wilson's method as used for the nitration product.

The nitration of phenyltrimethylarsonium picrate takes place with difficulty, and the best conditions found were as follows. A solution of the salt (4·0 g.) in 30 g. of nitric acid (*d* 1·52) was heated in a closed tube at 100° for 5 hours. During this process the picrate

ion is partly oxidised but the aryltrimethylarsonium ions only slightly so (less than 1·5%). The cooled solution was diluted with water (225 c.c.) containing 2·5 g. of picric acid and neutralised with sodium hydroxide solution (50 c.c.). The major portion of the nitration product was precipitated as picrate, and the remainder isolated, as in the foregoing experiments, acetone being used as solvent (yields, close to 98·5%). Preliminary experiments having shown that m-*nitrophenyltrimethylarsonium picrate* was the main product but that the residues contained isomerides, the bulk of the *m*-compound was separated in the pure state by crystallisation from water (94·6, 95·5, 95·5% of the total yield), and oriented by reduction and bromination. It forms orange-yellow needles, m. p. 180° (Found: C, 38·1; H, 3·0; As, 15·6. $C_{15}H_{15}O_9N_4As$ requires C, 38·2; H, 3·2; As, 15·9%). The residual mixtures (equivalent to 5·4, 4·5, 4·5% of the total) were reduced and titrated with bromine to obtain the meta-content (Found: 76, 74, 75%). The final figure for the proportion of *m*-compound is therefore 98·2% (mean). An approximate check was obtained by determining the solubility of the *m*-compound in solutions equivalent, except for the absence of the other isomerides, to those from which it was crystallised, and this gave 98·0%.

The nitration of benzyltrimethylarsonium picrate, the isolation of the products (yield, 100%), the partial separation (64·5%) of the para-compound, and the estimation of the *m*-isomeride in the unseparated mixture (Found: C, 40·1; H, 3·6%) were conducted as in the case of the corresponding phosphonium compound (Found: meta, 3·4, 3·4%). p-*Nitrobenzyltrimethylarsonium picrate* crystallises from acetone in orange-yellow needles, m. p. 166—168° (Found: C, 40·1; H, 3·8; As, 15·1. $C_{16}H_{17}O_9N_4As$ requires C, 39·7; H, 3·5; As, 15·5%).

Phenyltrimethylstibonium picrate is nitrated noticeably more readily than its phosphonium and arsonium analogues, and satisfactory conditions (yields, 99·5, 99·0%) were obtained by using the method for the former, except that the temperature was 0°. The isolation, partial separation of the *m*-isomeride (76·8, 73·0%), and the estimation of the *m*-isomeride (Found: meta, 85·4, 87·2%) were carried out by the method described for the arsonium compounds. m-*Nitrophenyltrimethylstibonium picrate* separates from water in needles, m. p. 203° (Found: C, 34·5; H, 2·9. $C_{15}H_{15}O_9N_4Sb$ requires C, 34·8; H, 2·9%).

In the absence of definitely comparative experiments, reference was not made in the introduction to Ingold and Shaw's suggestion (J., 1927, 2923) that the speed of nitration in *m*-substituting compounds should show a general decrease in a series in which the

proportion of *m*-derivative formed increases; nevertheless, the above qualitative observations give considerable support to this deduction.

We desire to record our thanks to the Royal Society for a grant in aid of this work.

THE UNIVERSITY, LEEDS. [*Received, April 2nd*, 1928.]

CLXIX.—*Diphenylamine*-p-*arsinic Acid.*

By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

LIEB and WINTERSTEINER (*Ber.*, 1928, **61**, 107) state that diphenylamine-*p*-arsinic acid has no melting point but decomposes somewhat sharply at 286° with foaming and blackening, and comment on the decomposition point, 265°, recorded by Burton and Gibson (J., 1926, 461).

No specimen of our original preparation being available, we have again prepared the acid and, using a somewhat different method of purification, now find that the melting or decomposition point previously recorded is too low. Diphenylamine-*p*-arsinic acid, about the purity of which there can be little doubt, begins to darken slightly at 287° and decomposes with foaming and blackening at 295—297°. The sodium salt is very sparingly soluble in 25% sodium hydroxide solution and can be obtained crystalline from an even more dilute solution of the alkali. We confirm the description of the magnesium salt and find that the easily prepared *hydrochloride* (m. p. 153—155° with decomp.) is convenient for identification purposes.

Incidentally we have characterised N-*acetyl*-p-*aminodiphenylamine* (p-*acetophenylamidoaniline*), which should have been described as a new compound in the former paper.

EXPERIMENTAL.

N-*Acetyl*-p-*aminodiphenylamine* (p-*Acetophenylamidoaniline*), $C_6H_5{\cdot}N(CO{\cdot}CH_3){\cdot}C_6H_4{\cdot}NH_2$.—
To a mixture of *p*-nitroacetyldiphenylamine (22 g.), alcohol (55 c.c.), water (55 c.c.), and acetic acid (5·5 c.c.), iron filings (22 g.) were cautiously added and the whole was gently heated under reflux. After the first vigorous reaction (during which external cooling with water is necessary) was over, the mixture was boiled for

4 hours. The product was mixed with a large volume of alcohol and the solution was filtered without pressure, evaporated to small volume, and diluted with water. The *base*, which was partly precipitated, was removed by repeated extractions with ether, recovered from the extracts by means of dilute hydrochloric acid, and precipitated by concentrated aqueous ammonia as an oil which quickly solidified; after cooling in the ice-chest, it was collected and recrystallised from alcohol or ligroin, separating in colourless, flat, elongated needles, m. p. 127—128° [Found: N, 12·3 (Gibson and Johnson), 12·7 (Burton and Gibson). $C_{14}H_{14}ON_2$ requires N, 12·4%]. On hydrolysis with boiling dilute hydrochloric acid it gave *p*-aminodiphenylamine, m. p. 73° after recrystallisation from ligroin (b. p. 60—80°) (compare Fischer and Wacker, *Ber.*, 1888, **21**, 2614).

Diphenylamine-p-*arsinic Acid.*—The conversion of *N*-acetyl-*p*-aminodiphenylamine (31·3 g.) into crude *N*-acetyldiphenylamine-*p*-arsinic acid by means of the Bart reaction was carried out as previously described (Burton and Gibson, *loc. cit.*). The crude acid was dissolved in warm 25% sodium hydroxide solution (60 c.c.), and the sodium salt obtained on cooling was filtered off as completely as possible, dried on porous earthenware, and dissolved in warm water. Acidification of the cooled solution precipitated a slightly discoloured solid, the m. p. of which, 260—271° (decomp.), showed that some hydrolysis of the *N*-acetyldiphenylamine-*p*-arsinic acid had taken place. Hydrolysis was completed by boiling the crude acid (10·5 g.) with alcohol (21 c.c.) and hydrochloric acid (21 c.c.) for 1 hour and pouring the product into water. The precipitated acid was dissolved in a boiling dilute solution of ammonia and the solution was decolorised with charcoal and filtered while hot. The filtrate was again heated to boiling, acidified with dilute hydrochloric acid, treated with charcoal, and filtered. Long, fine, colourless needles of diphenylamine-*p*-arsinic acid separated from the hot solution and were dried over potassium hydroxide in a vacuum desiccator. On being heated, the acid melted at 295—297° with frothing and blackening after slight darkening at 287° (compare Lieb and Wintersteiner, *loc. cit.*) (Found: N, 4·8; As, 25·8. Calc.: N, 4·8; As, 25·6%).

When a solution of diphenylamine-*p*-arsinic acid (0·95 g.) in hot alcohol (5·0 c.c.) and hydrochloric acid (20 c.c.) cools, the *hydrochloride* is deposited in small, colourless needles, m. p. 153—155° (decomp.). It turns somewhat green during the decomposition, which is preceded by slight darkening and shrinking at about 148° (Found: Cl, 10·8. $C_{12}H_{12}O_3NAs,HCl$ requires Cl, 10·75%). The sodium salt of diphenylamine-*p*-arsinic acid separates from its

solution in warm 25% sodium hydroxide on cooling in fine colourless needles. The solution has a marked tendency to remain supersaturated at the ordinary temperature.

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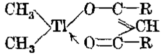
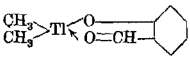
(UNIVERSITY OF LONDON), S.E. 1. [*Received, April 4th*, 1928.]

CLXX.—*Chelate Compounds of Thallium Dialkyl.*

By ROBERT CHARLES MENZIES, NEVIL VINCENT SIDGWICK, ERIC F. CUTCLIFFE, and JOHN M. C. FOX.*

THE known thallium dialkyl compounds are the salts of a strong univalent base $Alk_2Tl·OH$. We have prepared a series of derivatives of the dimethyl and diethyl bases with β-diketones, acetoacetic ester, and salicylaldehyde, in order to see whether the products were chelate compounds or salts. The presence of the two alkyl groups would give the thallium in a monochelate derivative the stable covalency of 4, and hence these bases should form such derivatives more readily than the alkali metals (see Sidgwick and Brewer, J., 1925, **127**, 2379). The compounds are easily formed by three reactions: (1) by double decomposition of the thallium dialkyl halides with thallous acetylacetone and similar compounds, (2) by the action of crude thallium dialkyl ethoxide (from the iodide or bromide and thallous ethoxide) on the diketone, (3) from thallium dialkyl carbonate and the diketone. The products, which are of the type Alk_2TlA (where A is the radical of the diketone or similar substance), have unusual properties. They are crystalline solids, which can be sublimed with ease under reduced pressure and are readily soluble in benzene and even in hexane. This indicates that they are not ionised, and so they may be assumed to be chelate compounds of types I and II (below):

(I.)   (II.)

In water on the other hand, with the exception of the benzoylacetone compounds, they are extremely soluble (which this structure would not lead us to expect), and they are clearly ionised, since the solution has a strong alkaline reaction (containing the salt of a strong base and a weak acid) and can be titrated quantitatively with acid and methyl-red, and it gives a precipitate of the sparingly

* This work was carried out independently by one of us (R. C. M.) at Bristol, and the rest at Oxford. The simplest course seems to be to publish the combined results as a single paper.

soluble thallium dialkyl iodide with potassium iodide. Thus in water they pass (like hydrochloric acid and stannic chloride) from the covalent to the ionised state. *Dimethyl* and *diethyl thallium benzoylacetone* dissolve in water very slowly even on boiling; their alcoholic solutions, however, remain clear on mixing with much water, and can then be titrated quantitatively; ether extracts from the diluted solution a substance which contains thallium dialkyl.

EXPERIMENTAL.

The thallium dialkyl halides were made by treating thallic chloride (dehydrated with copper sulphate) with excess of the Grignard reagent (Meyer and Bertheim, *Ber.*, 1904, **37**, 2051; Goddard, J., 1921, **119**, 672). The carbonate was obtained from the iodide by treatment with silver oxide and evaporation of the filtrate in an open vessel, or by double decomposition with thallous carbonate. The ethoxide was made by double decomposition with thallous ethoxide in absolute alcohol. These materials were used in the crude state. The thallium was estimated by titration with acid and methyl-red, or gravimetrically, after decomposition of the compound, either as chromate or as iodide (Meyer and Bertheim, *loc. cit.*; Goddard and Goddard, J., 1922, **121**, 488).

Thallium Dimethyl Acetylacetone.—Thallium dimethyl iodide (3·7 g.) was boiled in alcohol with thallous acetylacetone (3 g.) until a sample when filtered gave with potassium iodide a white precipitate free from yellow, thallous iodide. The hot liquid after filtering gave on cooling crystals of *thallium dimethyl acetylacetone*: more was obtained from the mother-liquor. Yield, 64%. M. p. (from benzene) 214—215° with some decomposition (Found: Tl as chromate 61·6, as iodide 61·1, by titration 61·0; C, 25·0; H, 3·9. $C_7H_{13}O_2Tl$ requires Tl, 61·3; C, 25·2; H, 3·9%). It is sparingly soluble in normal hexane and readily soluble in hot toluene and benzene, in methyl iodide (with which it seems to react slowly), and in warm carbon disulphide, the solution in which turns yellow on standing. The compound sublimes under atmospheric pressure, or better in a water-pump vacuum, at about 170°. It can also be made from the carbonate and acetylacetone in aqueous alcohol. Like all the other chelate compounds described in this paper, except those of benzoylacetone, it dissolves slowly in cold water and readily in hot. The solution has an alkaline reaction and gives a precipitate of thallium dimethyl iodide with potassium iodide.

Thallium diethyl acetylacetone was made in the same way from the bromide (4 g.) and thallous acetylacetone (3 g.) in absolute alcohol. Yield, 81% (Found: Tl as chromate 57·1, by titration

56·7; C, 30·7; H, 5·0. $C_9H_{17}O_2Tl$ requires Tl, 56·5; C, 29·9; H, 4·7%). It is soluble in *n*-hexane, cold toluene, and cold methyl iodide.

Thallium Dimethyl Benzoylacetone.—The reaction of the iodide with thallous benzoylacetone is very slow: the addition of ammonia (to increase the solubility of the iodide) leads to hydrolysis of the diketone and formation of thallium dimethyl acetate [Found: Tl, 69·0. Calc. for $(CH_3)_2Tl\cdot O\cdot CO\cdot CH_3$: Tl, 69·7%]. The desired *compound* can be made by heating the carbonate with benzoylacetone (without solvent) at 150°; but at 100° no reaction occurs. It is better prepared by boiling thallous ethoxide (20 g.) with thallium dimethyl bromide (25·15 g.) in alcohol (300 c.c.), evaporating the filtered solution to small bulk, adding benzoylacetone (13 g.) in the minimum of alcohol, and evaporating the mixture to dryness in a vacuum. Yield, 78·7%. It forms colourless crystals (from ligroin or by sublimation), m. p. 128—129°, sublimes at 120°/20 mm., and is readily soluble in cold methyl iodide, cold ether, hot hexane and hot benzene (Found: Tl by titration 51·5, as chromate 51·4; C, 36·3; H, 4·05. $C_{12}H_{15}O_2Tl$ requires Tl, 51·7; C, 36·4; H, 3·8%).

Thallium Diethyl Benzoylacetone.—A solution of thallium diethyl bromide (19 g.) and thallous ethoxide (12·5 g.) in alcohol (250 c.c.) was boiled, filtered, and evaporated to 20 c.c. Benzoylacetone (8 g.) was added: it dissolved in the hot solution, and on cooling, the required *compound* separated; after recrystallisation from ligroin it was obtained in 72% yield; m. p. 116—118°. It is soluble in methyl iodide, and very soluble in dry ether, from which it crystallises well. 100 G. of a solution in light petroleum (b. p. 40—60°), saturated at 19°, contain 3·29 g. (Found: Tl as chromate 46·5, by titration 48·6; C, 39·5; H, 4·6. $C_{14}H_{19}O_2Tl$ requires Tl, 48·3; C, 39·7; H, 4·5%).

Ethyl Thallium Dimethyl Acetoacetate.—The filtrate from thallous ethoxide (2·5 g.) and thallium dimethyl iodide (3·6 g.) was evaporated to dryness in a vacuum. To the residue, after solution in light petroleum, ethyl acetoacetate (1·3 g.) in light petroleum was added. 1·8 G. of the desired *compound* separated on cooling, and 0·6 g. was got from the mother-liquor. Yield, 66%. It forms thick, colourless prisms, m. p. 128—130°, soluble in the cold in *n*-hexane, benzene, toluene, and methyl iodide (Found: Tl as chromate 55·7, as iodide 56·1, by titration 56·3. $C_8H_{15}O_3Tl$ requires Tl, 56·3%). The compound is also formed by heating the carbonate with ethyl acetoacetate in benzene.

Ethyl Thallium Diethyl Acetoacetate.—Ethyl acetoacetate (4 g.) was added to the concentrated alcoholic solution (20 c.c.) from

thallium diethyl bromide (10·3 g.) and thallium ethoxide (7·5 g.), and the liquid evaporated to dryness, finally in a vacuum. The product is difficult to purify on account of its great solubility. It was boiled in ligroin with animal charcoal, and the clear brown filtrate on concentration to small bulk and cooling gave large, almost colourless crystals. Yield of pure product, 58%; m. p. 88—90°. In the cold the *compound* is readily soluble in *n*-hexane and very readily in dry ether and methyl iodide (Found: Tl by titration, 52·2, 52·1. $C_{10}H_{19}O_3Tl$ requires Tl, 52·35%).

Thallium Dimethyl Salicylaldehyde.—Salicylaldehyde (3·66 g.) and crude thallium dimethyl carbonate (7·9 g.) were boiled with pure benzene until the distillate was no longer cloudy, showing that the water formed in the reaction was removed. On cooling, part, and on concentration more, of the product separated. Yield, 63%. It forms lemon-yellow crystals, decomp. 200°, which can be sublimed at 160—170°/20 mm., and is easily soluble in benzene (Found: Tl as chromate 57·5, by titration 57·7; C, 30·5; H, 3·3. $C_9H_{11}O_2Tl$ requires Tl, 57·4; C, 30·4; H, 3·1%).

We wish to express our thanks to Messrs. Brunner Mond and Co. and to the Colston Research Committee for grants towards the expenses of this work.

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DYSON PERRINS LABORATORY, OXFORD.

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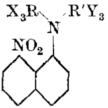
CLXXI.—*Molecular Dissymmetry Dependent on Restriction of Rotation about a Single Bond. Optically Active Benzenesulphonyl-8-nitro-1-naphthylglycine.*

By WILLIAM HOBSON MILLS and KENNETH ALLAN CALDWELL ELLIOTT.

IF, as appears probable (see, for example, Mills, *Chemistry and Industry Review*, 1926, **45**, 884), the molecular dissymmetry of certain diphenic acids, discovered by Kenner and his co-workers (J., 1922, **121**, 614, and subsequent papers) is due to obstruction of the rotation of the two benzene nuclei of the diphenyl molecule about a common axis by substituent groups in the 6- and 6′-positions, it should be possible to obtain evidence of a similar restriction of rotation in other classes of compounds and especially among the *peri*-disubstitution derivatives of naphthalene.

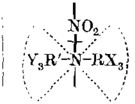
Thus, it seemed that in a compound of formula (I) derived from 1 : 8-nitronaphthylamine by replacement of the hydrogen atoms of the amino-group by two groups RX_3, $R'Y_3$, the rotation of the complex radical $X_3R—N—R'Y_3$ about the carbon-nitrogen bond *by which it is linked to the naphthalene nucleus must be restricted* by the presence of the nitro-group to a comparatively limited arc, as is indicated by the diagrams IIa, IIb (which are intended to represent I viewed from above, the thick line denoting the naphthalene nucleus viewed edge-wise).



(I.)

(IIa.)

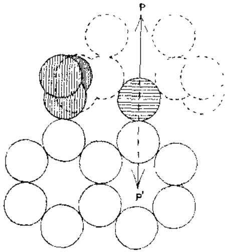
Mirror



(IIb.)

It is clear that if the rotation is in fact thus limited a compound *of the above type should exist in two enantiomorphous modifications*, and if, as is probable, their resistance to intertransformation through thermal agitation were considerable these modifications should show considerable persistence at moderate temperatures.

FIG. 1.



The probability that the rotation of the $-N(RX_3)(R'Y_3)$ complex will be obstructed by the nitro-group is perhaps more clearly indicated in the diagrammatic representation of the compound given in Fig. 1, which is constructed on the assumption that the atoms of carbon, nitrogen, and oxygen may be regarded for this purpose as spheres of diameter approximately 1·5 Å.U.

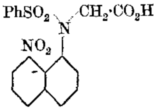
The ten carbon atoms of the naphthalene nucleus are shown in the lower half of the figure and the hydrogen atoms are omitted to simplify the diagram. The group of three vertically shaded spheres attached to the naphthalene nucleus in the 8-position represents a nitro-group; the horizontally shaded sphere represents the nitrogen atom of the $-N(RX_3)(R'Y_3)$ complex, and the $-RX_3$ and $R'Y_3$ groups are indicated with broken outlines. It will be seen that the nitro-group projects far into the space that the $-RX_3$ and

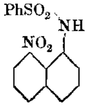
$-R'Y_3$ groups would sweep through if the complex $-N(RX_3)(R'Y_3)$ were rotated about the axis *PP'*. Unless, therefore, the diagram makes the *peri*-positions considerably too close together in comparison with the size of the substituent groups, the passage of the RX_3-group or $R'Y_3$-group over the obstacle presented by the nitro-group would require exceptional distortion of the molecule. It is, however, improbable that the *peri*-positions are more widely separated than represented in this diagram, in which the centres of the carbon atoms of the naphthalene nucleus are shown as 1·5 Å.U. apart, and lying with a regular hexagonal arrangement in one plane. If the molecule of naphthalene has a configuration which differs considerably from this, the difference will almost certainly be in the direction of greater compactness. *X*-Ray analysis would indicate that, at any rate in the crystalline state, the atoms of the naphthalene molecule are more closely packed than represented here; moreover, the structure of aromatic nuclei is not improbably related to that of the hexagonal nets in graphite in which the centres of the carbon atoms are only 1·45 Å.U. apart (Bernal, *Proc. Roy. Soc.*, 1924, *A*, **106**, 760).

A compound of the type under consideration should therefore exist in two enantiomorphous modifications of considerable persistence, as indicated by the formulæ (IIa) and (IIb).

The compound which we selected for testing these views experimentally was the benzenesulphonyl derivative of 8-nitro-1-naphthylglycine (III), the ester of which was readily prepared by the action of ethyl bromoacetate on the sodio-derivative of benzenesulphonyl-*8-nitro-1-naphthylamine* (IV), *there being no indication of appreciable* steric hindrance to the entry of the additional substituent group. The sulphonyl group in this compound serves to deprive the nitrogen

(III.)





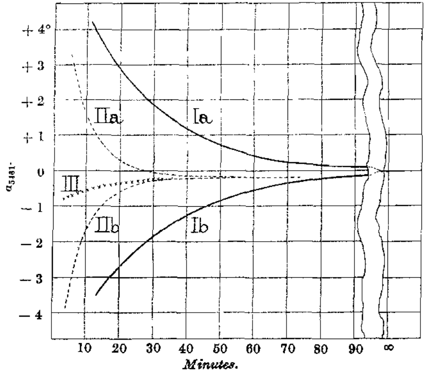
(IV.)

atom of any tendency to pass into the ammonium state and the carboxyl group gives the substance the power of forming salts with optically active bases needed for examining its resolvability into optical antipodes.

Experiments carried out with the brucine salt showed that the acid could in fact be obtained in two antimeric optically active forms. When equivalent quantities of the acid and brucine were mixed in acetone solution a brucine salt crystallised in more than 90% of the theoretical yield and this was the brucine salt of a

lævorotatory modification of the acid. For after its decomposition by extraction of its chloroform solution with sulphuric acid the resulting chloroform solution of the acid was strongly lævorotatory, but the lævorotation gradually disappeared in accordance with the unimolecular law as shown by curve Ib in Fig. 2. The time of half-change at 14·9° was 17 minutes and the average time of persistence of a molecule in either of the two modifications (IIa) or (IIb) was accordingly 25 minutes. The specific rotation, $[\alpha]_{5461}$, when first observed was − 242°, but as this observation was not made until 13 minutes after the salt had been added to the chloroform the

FIG. 2.



initial value of the specific rotation must have been considerably greater, probably at least − 400°.

Moreover chloroform solutions of this brucine *l*-acid salt showed mutarotation, the original strong lævorotation diminishing greatly as the acid component of the salt lost its activity. Thus in a typical experiment, the first reading (taken 4 minutes after bringing the salt into contact with chloroform) showed a rotation, α_{5461}, of − 3·86° and this fell steadily during 48 minutes at 15·5° to −0·19°, the final value reached after equilibrium had become established being − 0·18°. The average period of half-change in this experiment was 5 minutes; the racemisation of the acid is thus much more rapid when in combination with brucine than in the free state. The course of the mutarotation of this salt is shown in Fig. 2, curve IIb. The various

curves in this figure represent observed rotations of mercury green light for equimolecular solutions (0·00947M) in chloroform in a 4-dcm. tube plotted against the time in minutes after bringing the substance into contact with the solvent, the temperature being Ia, 15·3°; Ib, 14·9°; IIa, 15·5°; and IIb, 14·8°.

The *dextrorotatory form* of the acid was obtained in the following manner. The brucine *l*-acid salt was dissolved in methyl alcohol, in which it is easily soluble, but the solution soon deposited a new salt which is sparingly soluble in this solvent. The new salt has 3 molecules of water of crystallisation, the original salt having only 1, and whereas the new salt is less soluble than the original in methyl alcohol, it is much the more soluble in acetone.

Examination showed that this new salt was, as had been anticipated, the brucine salt of the *d*-acid. Its solution in chloroform, observed as soon as possible after preparation, was strongly dextrorotatory, $[\alpha]_{5461} + 103°$, and the rotation gradually sank (Fig. 2, curve IIa) with an average period of half-change of 5·2 minutes, reaching zero after 22 minutes, and then becoming negative; the equilibrium value finally attained was the same as that for the brucine salt of the *l*-acid.

By removing the brucine from a solution of the salt in chloroform a solution of the *d*-acid was obtained, the first observation, made 11 minutes after bringing the salt into contact with chloroform, giving the reading $\alpha_{5461} + 4·19°$ ($[\alpha]_{5461} + 287°$), and the rotation was seen to sink gradually according to the unimolecular law (Fig. 2, curve Ia), reaching zero (practically) in about 1½ hours. The temperature was 0·4° higher than in the corresponding experiment described for the *l*-acid and the time of half-change, 15·9 minutes, was accordingly somewhat shorter.

It has thus been established that benzenesulphonylnitronaphthylglycine can exist in two enantiomorphous modifications which possess a limited stability to thermal agitation. Since attempts to resolve nitrogen compounds of the type Nabc by methods similar to that used in this investigation have proved uniformly unsuccessful, it seems justifiable to disregard the possibility that the optical activity of this acid could arise from the presence of the possibly asymmetric nitrogen atom $N(C_{10}H_6·NO_2)(SO_2Ph)(CH_2·CO_2H)$. For similar reasons the possibility that it might be a consequence of the nonplanar configuration of the naphthalene molecule may also, we think, be considered out of the question.

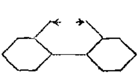
To obtain experimental confirmation of this (although we would not unduly stress the value of such negative evidence) we prepared and examined the corresponding compound in which the nitro-group in the 8-position was lacking, benzenesulphonyl-1-naphthyl-

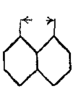
glycine. The brucine salt of this acid unfortunately could not be got to crystallise; quinine, however, gave a crystalline salt, but we could obtain no indication that the acid could be rendered optically active by this alkaloid.

It would seem, therefore, that there is no reasonable alternative to referring the molecular dissymmetry of benzenesulphonylnitronaphthylglycine to its most obvious cause—the restriction of the rotation of the $Ph{\cdot}SO_2{\cdot}N{\cdot}CH_2{\cdot}CO_2H$ complex about the bond linking it to the naphthalene nucleus by the obstruction presented by the 8-nitro-group.

The demonstration that this *peri*-disubstitution derivative of naphthalene can exist in optically active modifications evidently serves to confirm the theory that the molecular dissymmetry of the substituted diphenic acids likewise has its origin in steric restriction of rotation.

The naphthalene derivative differs considerably, however, from the diphenic acids in the readiness with which it undergoes autoracemisation; the optical stability of the diphenic acids is much greater (Christie and Kenner, J., 1922, **121**, 614; Bell and Robinson, J., 1927, 2234; Kuhn and Albrecht, *Annalen*, 1927, **455**, 272; **458**, 221). This may be due in part to differences in rigidity of the bonds concerned—in the naphthalene derivative it is a tervalent nitrogen atom that forms the hub of the rotating system—but the chief cause doubtless lies in the fact that the distance between substituent atoms is greater when they are in the naphthalene *peri*-relationship than when in the 6- and 6′-positions (at closest approach) of the diphenyl molecule. Some rough indication of the relationship between these distances may perhaps be obtained by assuming a regular hexagonal arrangement for the carbon atoms of the benzene nucleus. The distances would then be, as the accompanying diagrams show, in the ratio of $1 : \sqrt{3}$, or $1 : 1{\cdot}73$. The temperature





coefficient (for 10°) of the racemisation velocity of the brucine salts in chloroform solution, calculated from the velocity coefficients at 14·8° and 0·6°, was found to be 3·27. This corresponds with a heat of activation of 18,500 cal.

In consequence of their ready autoracemisation the brucine salts of the optically active modifications of the acid are evidently obtained as the result of processes of activation rather than of resolution, similar to those observed, for example, by Pope and

Peachey (P., 1900, **16**, 116) with methylethylpropyltin camphorsulphonate, and by Mills and Bain (J., 1910, **97**, 1866) with the morphine and quinine salts of the oxime of *cyclo*hexanone-4-carboxylic acid.

The acid can also be rendered optically active by brucine in another way in which no separation of a solid phase is involved. When equivalent quantities of brucine and the inactive acid are dissolved separately in chloroform and the two solutions then mixed, the initial lævorotation of the mixture, due to the brucine, is observed to fall gradually to an equilibrium value as shown diagrammatically in Fig. 2, curve III. The amount of change depends on the temperature, being greater at lower temperatures. In an experiment carried out at 1° the lævorotation fell in a little over 1½ hours to 28% of the value first observed. The most probable cause of this mutarotation was partial activation of the acid; though slowness of salt formation in chloroform, which, however, is scarcely to be expected, would give rise to an effect of the kind observed, brucine being much more strongly lævorotatory in the free state than in its salts; slow solvation of the salt also might cause mutarotation. It was possible to show, however, by direct experiment that the phenomenon was actually due to the first of these causes. A chloroform solution of the salt was allowed to attain equilibrium at 0°, and the salt was then decomposed by extracting the solution with dilute sulphuric acid, whereby the brucine was removed and a chloroform solution of the acid was obtained. This solution showed a dextrorotation, similar in magnitude to the fall which had taken place in the lævorotation of the salt, and this rotation gradually fell to zero in accordance with the unimolecular law. The mutarotation must therefore have been due to the establishment of an equilibrium in which an excess of brucine *d*-acid salt was present. The interaction between brucine and the un-nitrated acid, benzenesulphonyl-1-naphthylglycine, was examined in a similar way. Here no trace of mutarotation was observed: the rotation had a constant value which was very nearly the same as the initial value for the brucine salt of the inactive nitro-acid. We regard this difference between the two acids as evidence of some weight that the molecular dissymmetry of the nitro-acid is determined by the nitro-group in the manner suggested and is not due to some other cause.

Since in a solution of the salt the brucine can scarcely have any directive effect on the free acid or on the acid-ion produced by dissociation, it would seem that the inequality of the amounts of the brucine *d*-acid salt and brucine *l*-acid salt present at equilibrium must be due primarily to differences in properties of the undissociated forms of these salts. There must be a difference between the

velocity coefficients of partial racemisation of the undissociated salts, and from the presence of an excess of *d*-acid salt in the equilibrium it is to be inferred that the coefficient for that salt is smaller than that for the brucine *l*-acid salt. The constants of dissociation of the two salts into ions (as well as into acid and base) will also differ to a greater or less extent, for it is evident that the ion of a dissymmetric base may fit more closely to one of the antimeric ions of a dissymmetric acid than to the other. Since the degree of dissociation in chloroform may be assumed to be small, the effect of this on the equilibrium will probably be smaller than that of the inequality of the velocity coefficients of partial racemisation and will be dependent on the relation between the velocity of intertransformation of the *d*- and *l*-free acids and of their ions and the velocities of intertransformation of the undissociated forms of the two salts.* The behaviour of these brucine salts is clearly analogous to that of the hydroxyhydrindamine salts of chlorobromomethanesulphonic acid and chlorobromoacetic acid described by Read and McMath (J., 1925, **127**, 1572; 1926, 2183).

It is evident that the occurrence of molecular dissymmetry dependent on obstructed rotation is also to be expected in other classes of compounds in which similar spatial relationships exist. The investigation of quaternary salts of appropriate 8-substitution derivatives of quinoline is being undertaken from this point of view.

EXPERIMENTAL.

1-*Benzenesulphonamido-8-nitronaphthalene* (IV).—An excess (nearly 1½ equivs.) of benzenesulphonyl chloride dissolved in anhydrous pyridine was added to a pyridine solution of 8-nitro-1-naphthylamine † (Meldola and Streatfeild, J., 1893, **63**, 1055) and the mixture was left over-night. The liquid was largely diluted with water, made alkaline with sodium hydroxide, filtered, and then acidified with hydrochloric acid. The *benzenesulphonyl* derivative thus precipitated crystallised from alcohol in colourless needles, m. p. 198—199° (Found: C, 58·4; H, 3·6. $C_{16}H_{12}O_4N_2S$ requires C, 58·5; H, 3·7%). Yield, 81%.

* The ratio (p) of the quantities of the *d*- and *l*-acid salts present in solution at equilibrium is easily shown to be given by the equation

$$p = \frac{k_L + a_L(k - k_L)}{k_D + a_D(k - k_D)},$$

where a_D and a_L are the degrees of dissociation of the brucine *d*-acid and *l*-acid salts, k_D and k_L the velocity coefficients of racemisation for the undissociated parts of these salts, and k the velocity coefficient of racemisation for the dissociated part.

† A product melting at 90—91° was found to be sufficiently pure to give a pure benzenesulphonyl derivative.

1-*Dibenzenesulphonamido*-8-*nitronaphthalene*,

$$NO_2\cdot C_{10}H_6\cdot N(SO_2Ph)_2,$$

was formed as a by-product and was separated on filtering the alkaline solution. It crystallises from much boiling water in short needles, m. p. 199°, mixed m. p. with the monosulphonyl derivative about 170° (Found: S, 13·5. $C_{22}H_{16}O_6N_2S_2$ requires S, 13·7%). The quantity produced was about 7% of the nitronaphthylamine used.

Ethyl N-*Benzenesulphonyl*-8-*nitro*-1-*naphthylaminoacetate*.—An absolute alcoholic solution of sodium ethoxide (1 equiv.) was added slowly to a suspension of benzenesulphonamidonitronaphthalene in absolute alcohol, and ethyl bromoacetate (slightly more than 1 equiv.) added to the resulting solution of the sodium salt. On cooling after boiling over-night, tufts of short needle-like crystals were formed, which, recrystallised from alcohol, melted at 173° (Found: C, 58·2; H, 4·4. $C_{20}H_{18}O_6N_2S$ requires C, 58·0; H, 4·4%). Yield, 75%.

N-*Benzenesulphonyl*-8-*nitro*-1-*naphthylglycine*.—The ester (12 g.) was dissolved in acetic acid (135 c.c.), dilute sulphuric acid (1 : 12 vols.; 60 c.c.) added, and the mixture kept at the boiling temperature over-night. It was then diluted largely, the *acid* redissolved by adding ammonia, the solution filtered, and the acid precipitated with hydrochloric acid. It crystallised from dilute acetic acid, after being decolorised with charcoal, in needles, m. p. 214° (Found: C, 55·6; H, 3·8; N, 7·1; S, 8·2. $C_{18}H_{14}O_6N_2S$ requires C, 55·9; H, 3·7; N, 7·25; S, 8·2%). Yield of recrystallised product, 81%.

Brucine 1-*Benzenesulphonyl*-8-*nitro*-1-*naphthylaminoacetate*.—When solutions in acetone of equivalent quantities of the inactive acid and brucine are mixed, the salt of the *l*-acid is deposited after a short time as a fine, heavy powder, m. p. 195—196°. It contains $1H_2O$ (Found: H_2O, 2·1. $C_{41}H_{40}O_{10}N_4S,H_2O$ requires H_2O, 2·25%). Yield, 98 %.

A solution of the salt in chloroform containing 0·378 g. of the monohydrate in 50 c.c. showed at 15·5° the following rotations ($l = 4$), the first observation being made 4 minutes after the salt had been first wetted:

t.	α_{5461}.	k.	t.	α_{5461}.	k.
0	−3·86°	—	13	−0·73°	0·064
3	−2·55	0·064	16	−0·56	0·062
3·5	−2·30	0·066	20·5	−0·39	0·061
4	−2·16	0·067	23·5	−0·33	0·059
5·5	−1·84	0·063	26·5	−0·29	0·057
6	−1·60	0·069	30	−0·27	0·054
7	−1·41	0·068	34·5	−0·23	0·054
8	−1·29	0·065	38	−0·21	0·055
9	−1·13	0·065	48	−0·19	0·054
11	−0·91	0·064	∞	−0·18	—

In this and in the following tables the numbers in the first column give the time (minutes) from the first observation; those in the second column are observed rotations of mercury green light; and those in the third column are calculated with the usual formula for the velocity coefficient of a unimolecular reaction, using decadic logarithms.

Mutarotation of l-*Benzenesulphonyl-8-nitro-1-naphthylglycine.*—A chloroform solution of the brucine *l*-acid salt containing 0·378 g. of salt in 50 c.c. was extracted twice with dilute (1 : 6) sulphuric acid (30 c.c.) to remove the brucine. The filtered chloroform solution of the acid obtained showed at 14·9° the following rotations ($l = 4$), the first reading having been made 13 minutes after the first wetting of the salt with chloroform :

t.	a_{5461}.	k.	t.	a_{5461}.	k.
0	−3·50°	—	30·8	−1·06°	0·0170
2·2	−3·18	0·0190	37·6	−0·75	0·0180
5	−2·91	0·0161	45	−0·55	0·0182
7	−2·63	0·0179	49·7	−0·46	0·0181
9·3	−2·44	0·0166	54·5	−0·39	0·0179
11	−2·26	0·0174	60·7	−0·30	0·0180
14·4	−2·00	0·0170	71	−0·18	0·0188
20·6	−1·55	0·0173	85·6	−0·15	0·0167
25·5	−1·31	0·0169	∞	−0·02	—

Brucine d-*Benzenesulphonyl-8-nitro-1-naphthylaminoacetate.*— The brucine salt of the *l*-acid (4 g.) was dissolved in boiling methyl alcohol (400 c.c.) and the solution on cooling deposited the brucine salt of the *d*-acid (3 g.) as colourless needles containing 3 molecules of water of crystallisation (Found : H_2O, 6·4. $C_{41}H_{40}O_{10}N_4S,3H_2O$ requires H_2O, 6·5%). It is soluble in hot acetone and, on standing, the solution deposits the brucine salt of the *l*-acid as a colourless powder, m. p. 195—196°.

A solution of the salt in chloroform containing 0·395 g. of the trihydrate in 50 c.c. showed at 14·8° the following rotations of the mercury green light ($l = 4$), the first observation being made 5 minutes after the salt had been wetted :

t.	a_{5461}.	k.	t.	a_{5461}.	k.
0	+3·25°	—	14·3	+0·31°	0·059
2	+2·43	0·059	21·5	+0·02	0·057
3	+2·04	0·063	26	−0·08	0·059
4	+1·78	0·061	30	−0·11	0·053
5·5	+1·43	0·060	33·5	−0·13	0·055
7·3	+1·03	0·059	36·7	−0·15	0·056
8·5	+0·86	0·061	41	−0·16	0·055
10·7	+0·62	0·059	∞	−0·18	—

On repeating the experiment at a lower temperature (0·6°), the same quantities being used, the following observations of the mutarotation of the salt were made, the first reading being taken $11\frac{1}{2}$ minutes after bringing the salt into contact with chloroform :

t.	α_{5461}.	k.	t.	α_{5461}.	k.
0	+3·85°	—	27	+1·86°	0·0108
2	+3·66	0·0102	32	+1·59	0·0110
3·7	+3·47	0·0115	37·5	+1·34	0·0111
6	+3·30	0·0105	45·8	+1·03	0·0112
8·5	+3·07	0·0109	54·5	+0·80	0·0110
10·5	+2·92	0·0107	64	+0·60	0·0109
14·7	+2·66	0·0102	84	+0·46	0·0093
19	+2·36	0·0104	∞	−0·22	—
23·5	+2·06	0·0107			

Mutarotation of d-*Benzenesulphonyl*-8-*nitro*-1-*naphthylglycine*.—A chloroform solution of the *d*-acid was obtained by removal of the brucine from a solution (50 c.c.) of the brucine *d*-acid salt (0·395 g.) in chloroform by extraction with dilute sulphuric acid. The solution showed at 15·3° the following rotations ($l = 4$), the first having been made 11 minutes after the salt had been wetted :

t.	α_{5461}.	k.	t.	α_{5461}.	k.
0	+4·19°	—	34·9	+0·89°	0·0188
2·7	+3·74	0·0179	45·5	+0·56	0·0185
4·5	+3·47	0·0180	53	+0·35	0·0193
7·3	+3·06	0·0184	61	+0·23	0·0194
10	+2·71	0·0187	69·3	+0·14	0·0195
13·5	+2·30	0·0190	74·5	+0·11	0·0191
16·5	+2·06	0·0184	84·5	+0·04	0·0198
19·7	+1·78	0·0185	∞	−0·05	—
22·5	+1·53	0·0191			
27·7	+1·23	0·0187			

The final slight lævorotation was due to a trace of unremoved brucine.

Activation of the Acid by Brucine in Chloroform Solution.—A solution (25 c.c.) of the inactive acid (0·183 g.) in chloroform and the same volume of a chloroform solution of brucine (0·221 g.) were cooled to 0° and mixed and the mixture was observed in a jacketed 4-dcm. tube, the temperature rising during the experiment from 0·7° to 1·5°. The following readings were made :

t	0	3	8	15	22	25	30
α_{5461}	−0·78°	−0·76°	−0·70°	−0·65°	−0·55°	−0·52°	−0·47°
t	35	42·6	55	68	80	92	∞
α_{5461}	−0·42°	−0·39°	−0·33°	−0·30°	−0·26°	−0·23°	−0·22°

The equilibrium varies considerably with the temperature; when the temperature was allowed to rise to 14° the rotation fell to − 0·43°. The equilibrium rotation is also affected by the addition of an excess of acid; in an experiment carried out at 14·5° with the same quantities as above, an equilibrium rotation of − 0·34° was observed, and this rose to − 0·11° after an additional 0·1 g. of acid had been dissolved in the solution; this may indicate a slight dissociation of the salt in chloroform.

That the rise of rotation was due to the production of an excess of *d*-acid in the solution was proved as follows : A chloroform

solution (50 c.c.) of the inactive acid (0·183 g.) and brucine (0·211 g.) was kept in ice for 3 hours to allow equilibrium to become established and the brucine was then removed as rapidly as possible by extraction with ice-cold dilute sulphuric acid. A little acetone (6 c.c.) was added to keep the acid in solution and the chloroform–acetone solution was observed at 1·2°, the first reading being made 11 minutes after addition of the sulphuric acid. The following observations were made:

t	0	4·3	16	22	32·5
α_{5461}	+0·59°	+0·55°	+0·49°	+0·46°	+0·41°
t	63	93	173	∞	
α_{5461}	+0·37°	+0·33°	+0·24°	−0·01°	

Ethyl Benzenesulphonyl-1-naphthylaminoacetate.—This was prepared from benzenesulpbon-1-naphthylamide (Witt and Schmidt, *Ber.*, 1894, **27**, 2371), which we obtained, however, similarly to the nitro-derivative, from 1-naphthylamine (9·5 g.), benzenesulphonyl chloride (11·8 g.), and pyridine (75 c.c.); m. p. 170—171° (Witt and Schmidt give 166—167°).

Benzenesulphon-1-naphthylamide (9 g.) was dissolved in a solution of sodium ethoxide, made from sodium (0·73 g.) and alcohol (110 c.c.), ethyl bromoacetate (5·4 g.) was then added, and the mixture left over-night. The product, isolated in the same way as the nitro-derivative, formed colourless, flat, rhombic prisms, m. p. 89°; yield of recrystallised substance, 83·5% (Found: S, 8·7. $C_{20}H_{19}O_4NS$ requires S, 8·7%).

Benzenesulphonyl-1-naphthylglycine.—The hydrolysis of the ester was carried out similarly to that of the nitro-ester. The ester (7·4 g.) was boiled with a mixture of acetic acid (100 c.c.), water (50 c.c.), and dilute sulphuric acid (20 c.c.). The resulting acid, crystallised from dilute acetic acid, formed short needles, m. p. 188—189°; yield, 89% (Found: C, 63·4; H, 4·5; N, 4·4; S, 9·3. $C_{18}H_{15}O_4NS$ requires C, 63·3; H, 4·4; N, 4·1; S, 9·4%).

When equivalent quantities of the acid and quinine dissolved in acetone are mixed, the quinine salt is rapidly deposited in almost theoretical amount. It melts at 230° and is unaltered in melting point after crystallising from a large volume of methyl alcohol. Solutions of this salt in chloroform showed no mutarotation, neither could any indication be obtained that the acid could be activated by brucine. The acid (0·162 g.) and brucine (0·221 g.) were each dissolved separately in chloroform (25 c.c.) and the two solutions were mixed at 0°. On examination of the solution in the polarimeter no mutarotation conld be detected, the rotation remaining quite constant at − 0·94° at 1°.

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CLXXII.—*The Higher-boiling Constituents of the Essential Oil of Hops.*

By A. CHASTON CHAPMAN.

IN my earlier work on the essential oil of hops (J., 1895, **67**, 54) comparatively small quantities of the oil were used, and consequently the amount of high-boiling fractions, that is, of fractions boiling at temperatures above the boiling point of humulene, was so small as to render their examination impossible.

Through the kindness of Messrs. White, Tomkins and Courage, Ltd., I have had placed at my disposal a quantity of these high-boiling fractions obtained by them in the rectification of hop oil on the large scale. This residue consisted of a dark, viscous oil having an odour differing appreciably from that of ordinary hop oil. Having been dried by heating gently in a current of carbon dioxide, it was distilled under a pressure of 4 mm., and three fractions were collected, b. p. 80—150°, 150—180°, and 180—210° respectively. On further fractional distillation the following seven fractions were obtained:

Fraction.	B. p.	$n_D^{20°}$.	$d_{20°}^{20°}$.	Fraction.	B. p.	$n_D^{20°}$.	$d_{20°}^{20°}$.
1	87— 97°	1·4769	0·8948	5	140—150°	1·4960	0·9389
2	97—110	1·4900	0·9091	6	150—180	1·4969	0·9469
3	110—130	1·4940	0·9328	7	180—200	1·4975	0·9560
4	130—140	1·4950	0·9379				

Fraction No. 1 (b. p. 87—97°).—This reacted strongly with sodium and was found to contain a considerable proportion of saponifiable substances. It was therefore heated with a slight excess of alcoholic potash, and the unsaponifiable oil which remained was separated, dried, and redistilled, the boiling point rising from 65° to 120°. This oil was then esterified in the usual manner by treatment with phthalic anhydride, the portion which resisted esterification being separated and submitted to a fractional distillation. Three fractions were obtained boiling at 76—85°, 85—90°, and 90—98°/4 mm., respectively. Fraction No. 1 reacted vigorously with sodium and on the addition of semicarbazide gave a small quantity of a crystalline substance which, after recrystallisation from light petroleum, melted at 98° (Found: C, 66·8; H, 10·1; N, 17·0. $C_{14}H_{25}ON_3$ requires C, 66·9; H, 9·9; N, 16·8%). From the above formula it would appear that the reacting carbonyl compound must have had the formula $C_{13}H_{22}O$. The molecular weight of the substance regenerated from the semicarbazone was found by the cryoscopic method to be 190 ($C_{13}H_{22}O$ requires *M*, 194). This substance had a pleasant odour, and b. p. 74—76°/3 mm., $d_{20°}^{20°}$ 0·8861, $n_D^{20°}$ 1·485, and $[\alpha]_D$ − 0·4°. It appears to be a new ketone, for which I suggest the name *luparone*,

but unfortunately the quantity obtained was so small that furthe examination was impossible.

Fraction No. 2 (b. p. 97—110°).—This consisted almost entirel of humulene, and the small amount of liquid having a higher boilin point than that of hnmulene was added to the next fractions.

Fractions Nos. 3, 4 *and* 5 (b. p. 110—150°).—The general character istics of these three fractions having proved to be similar, they wer mixed and submitted to further fractionation. Fonr fractions wer obtained boiling from 122—174°/3 mm. The densities (20°/20° of these ranged from 0·9310 to 0·9398, the refractive indices (20° from 1·4925 to 1·4950, and the rotations from + 2·3° for th lowest fraction to − 1·2° for the highest.

As all these fractions reacted with alkali, it was thought that ester or other saponifiable substances might be present, and the mixe fractions were therefore heated with a slight excess of alcoholi potash. Investigation showed that the disappearance of the alkal was due not to the hydrolysis of esters, but to the decompositio of some substance with the formation of an acid. Treatment wit potash was therefore discontinued, and the portion which ha resisted the action of the alkali was submitted to further examination A portion of this was acetylated quantitatively and was found t contain an alcohol. The remainder was heated for 8 hours at 140 with an excess of phthalic anhydride in an atmosphere of carbo dioxide. The mixture was cooled and extracted with a dilute solu tion of caustic soda and the aqueous portion was evaporated an heated with an excess of alcoholic potash. The alcohol so obtaine was again treated in the same manner with phthalic anhydride and after separation as before was distilled. The greater part boiled at 125—128°/3 mm. and had the following properties. It was a very viscous, colourless, odourless liquid which showed no tendency t crystallise even when cooled in a mixture of solid carbon dioxid and ether; it had $d_{20°}^{20°}$ 0·9738, $n_D^{20°}$ 1·5023, $[\alpha]_D^{20°}$ − 3·7° (Found : C, 81·7; H, 11·1; *M*, cryoscopic in benzene, 225. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9%; *M*, 220). When it was heated with phenyl-carbimide, a urethane was obtained which crystallised from dilute alcohol in small needles, m. p. 157° (Found : C, 77·6; H, 8·6; N, 4·3. $C_{22}H_{29}O_2N$ requires C, 77·8; H, 8·5; N, 4·1%). The alcohol was unsaturated, uniting readily with an amount of bromine corresponding with the presence of one ethylenic linkage. It also appears to be a new compound, for which I suggest the name *luparenol*. This name and the names of two other new compounds described in this paper have been based upon a Spanish word *lupar* (the hop) in order to avoid confusion with various compounds, the names of which have been derived from the Latin designation *humulus lupulus*.

The liquid remaining after the removal of the unsaturated sesquiterpene alcohol gave an intense red colour with ferric chloride, and apparently therefore contained a phenolic substance. It was, however, very difficult to isolate this, since it formed with alkali a salt which decomposed on treatment with water. In addition to this, there was evidence of the presence of a substance having the properties of a tertiary alcohol, from which the phenolic substance could not be completely separated. Attempts to prepare derivatives by treatment with ordinary reagents failed to give any result, and it was therefore decided to resort to the preparation of the silver derivative. The phenol was purified as far as possible by further treatment with phthalic anhydride and subsequent fractionation and from the purified substance a silver salt was prepared by the addition of an alcoholic solution of silver nitrate. An oily liquid resulted which solidified after a few hours. This was separated, washed, and treated with dilute sulphuric acid for the regeneration of the phenol. On steam distillation, the phenolic substance obtained was a pale yellow, mobile oil, having a slight but pleasant odour, b. p. 122—124°/2 mm., $d_{20°}^{20°}$ 0·9170, and $n_D^{20°}$ 1·4942. It was optically inactive (Found: C, 76·6; H, 10·6; *M*, cryoscopic in benzene, 246. $C_{16}H_{26}O_2$ requires C, 76·8; H, 10·4%; *M*, 250). For this substance, which has the general characters of a phenolic ether, I suggest the name *luparol*. It gave an intense red coloration with ferric chloride in alcoholic solution. When boiled for some hours with 50% aqueous potash, it underwent gradual decomposition with the formation of *iso*valeric acid and, among other products, a phenol. *iso*Valeric acid appeared also as the chief product when the substance was oxidised with aqueous potassium permanganate. A very small quantity of the phenol was obtained, b. p. 115—117°/4 mm., $d_{20°}^{20°}$ 0·9448, $n_D^{20°}$ 1·4670 (Found: C, 73·2; H, 9·2. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%). The molecular weight in benzene was, however, considerably higher than that required by the above formula.

Fractions Nos. 6 *and* 7 (b. p. 150—200°).—These, which were very small fractions, gave an intense red coloration with ferric chloride and were found to consist chiefly of the phenolic ether mixed with a proportion of the sesquiterpene alcohol. There was also a small quantity of some very viscous compound which probably consisted of the polymerisation products of myrcene.

The original oil contained a certain amount of free acid, which was removed by shaking with dilute aqueous potash before the investigation above described was commenced. These acids were liberated, and distilled. Silver salts having been prepared and analysed, the greater part was found to consist of *iso*valeric acid,

but other acids—which owing to the small quantity of the material available could not be identified—were present in smaller proportions.

It seems very probable from these results that the *iso*valeric acid, and possibly also the other acids mentioned above, had been formed partly, at least, as the result of the oxidation of the phenolic ether, and this may well account for the presence of this acid in old hops.

The difficulties experienced in separating and purifying the substances described above have been considerable, owing chiefly to the very small proportions in which they occur in the essential oil, and the work would have been impossible but for the kind co-operation of Messrs. White, Tomkins and Courage, Ltd. These substances are, in fact, frequently present in nothing more than traces in commercial hop oil, and at the most occur in some specimens to the extent of a few units %. Notwithstanding this, there can be little doubt that they do at times modify the odour of the oil.

I desire to offer my best thanks to Mr. Gerald Bishop, M.Sc., A.I.C., for his valuable assistance.

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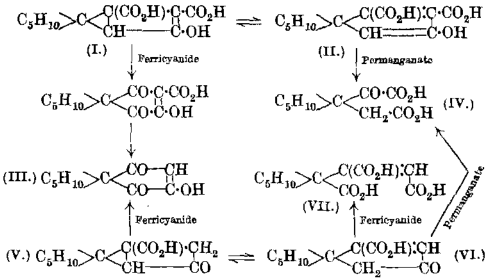
8 DUKE STREET, E.C. 3. [*Received, April 14th*, 1928.]

CLXXIII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part IX. The Effect of the* spirocyclo*Pentane Grouping on the Five-carbon Intra-annular Tautomeric Nucleus.*

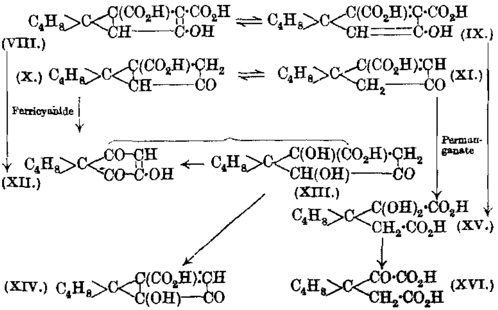
By FRANK ROBERT GOSS.

EXPERIMENTS on the oxidation by alkaline ferricyanide of the cyclohexane*spirodicyclo*pentene acid (I, II) carried out by Ingold, Seeley, and Thorpe (J., 1923, **123**, 853) resulted in the production of a cyclic 1 : 4-diketone (III). The quinonoid character of this compound anticipated on the basis of the semi-aromatic character of the type of system discussed in these communications was substantiated by Hassell and Ingold (J., 1926, 1836), who showed that its monoxime is also a nitroso-compound having a close similarity to *p*-nitrosophenol. Whereas the formation of the diketone (III) is attributed to form (I) of the parent acid, oxidation with permanganate yielded as main product an α-ketoglutaric acid (IV) evidently derived from form (II) only. The monobasic ketonic

acids (V, VI) showed stronger evidence of the monocyclic phase. Not only did permanganate give the ketoglutaric acid (IV), but ferricyanide yielded, in addition to the 1 : 4-diketone (III), a substituted aconitic acid (VII) obviously derived from form (VI).



The relationship between these results and those obtained in the *gem*-dimethyl series has already been discussed (Ingold, Seeley, and Thorpe, *loc. cit.*) and the object of this paper is to place on record the results which have been obtained in a similar investigation of the corresponding acids of the *cyclo*pentane*spirodicyclo*pentene series.



The dibasic acid (VIII, IX) (Ingold, Lanfear, and Thorpe, J., 1923, **123**, 3140) closely resembles its *cyclo*hexane analogue in yielding with ferricyanide only a cyclic 1 : 4-diketone (XII) and with

permanganate only oxalic acid and a substituted αα-dihydroxyglutaric acid (XV), which on dehydration gives an α-ketoglutaric acid (XVI) analogous to that obtained in the investigation already summarised. The chief divergence in behaviour of the *cyclo*pentane compounds emerged during the study of the monobasic ketonic acid (X, XI). This acid, like its *cyclo*hexane analogue, yielded a 1 : 4-diketone (XII) on oxidation with ferricyanide, but the by-product was not an aconitic acid (indeed no such acid has been encountered in the course of these experiments), but a monobasic hydroxyketonic acid (XIV), which may be assumed to have been formed by elimination of water from the dihydroxyketonic acid (XIII), a probable intermediate in the production of (XII).

Potassium permanganate gave a mixture of the αα-dihydroxyglutaric acid (XV) and the corresponding ketoglutaric acid (XVI). It is thus evident that the unsaturated phase (XI) is certainly present, but since substituted aconitic acids have been shown to be the normal products of oxidation with ferricyanide of forms analogous to (XI) in the cases hitherto examined, the non-appearance of an aconitic acid in this series is remarkable, and suggests that the importance of the unsaturated phase is less in this series than in the *cyclo*hexane series. This conclusion is consistent with the relative order which has been established for the effects of the *gem*-dimethyl group and the *spirocyclo*pentane and *spirocyclo*hexane rings on the basis of other investigations (Becker and Thorpe, J., 1920, **117**, 1579; Lanfear and Thorpe, J., 1923, **123**, 1683; Ingold, Lanfear, and Thorpe, *ibid.*, p. 3140).

EXPERIMENTAL.

(A) *Oxidation of* 5-cyclo*Pentane*spirodicyclo*pentan*-3-*one*-1-*carboxylic Acid* (5-cyclo*Pentane*spirocyclo*penten*-3-*one*-1-*carboxylic Acid*) (X, XI) *with Potassium Ferricyanide*.—The monobasic acid (10 g.) was added to a solution of 200 g. of potassium ferricyanide and 48 g. of potassium carbonate in 800 c.c. of water, which was kept for 168 hours at 60°, then cooled, acidified with hydrochloric acid, and extracted with ether. The solid product obtained from the ether was separated into two fractions (4·2 g., m. p. 140°; 0·25 g., m. p. 85—95°) by crystallisation from ether. The larger fraction was treated with methyl alcohol and sulphuric acid, and the product separated into three fractions by crystallisation from ether. The first fraction, forming the bulk of the material, consisted of nearly pure 3-*methoxy*-5-cyclo*pentane*spirocyclo*penten*-1 : 4-*dione*, which crystallised in needles, m. p. 65° (Found: C, 66·9; H, 6·6. $C_{10}H_{12}O_3$ requires C, 66·6; H, 6·7%). This was reconverted into 5-cyclo*pentane*spirocyclo*penten*-3-*ol*-1 : 4-*dione* (XII) by boiling for

2 hours with hydrochloric acid; the dione was obtained as a yellow, crystalline precipitate on cooling, which crystallised from xylene or water in needles, m. p. 154° (Found: C, 65·4; H, 5·8. $C_9H_{10}O_3$ *requires C, 65·0; H, 6·1%). This compound gives a cherry-red colour with alcoholic ferric chloride,* liberates carbon dioxide from sodium bicarbonate solution, and discharges the colour of alkaline permanganate. The second fraction of the esterification product, consisting of *methyl* 5-cyclo*pentane*spirodicyclo*pentan*(or cyclo-*penten*)-4-*ol*-3-*one*-1-*carboxylate*, crystallised in needles, m. p. 145° (Found: C, 62·7; H, 6·9. $C_{11}H_{14}O_4$ requires C, 62·8; H, 6·7%). The third fraction, which did not solidify, gave the same figures for carbon and hydrogen content on microcombustion as a liquid product obtained by converting the smaller fraction of the original oxidation product into its methyl ester. The two liquids, therefore, were mixed and on distillation in a good vacuum were separated into two fractions, (*a*) b. p. 145°/1 mm. and (*b*) b. p. 165°/1 mm. Fraction (*a*) on hydrolysis with hydrochloric acid gave a product which, after recrystallisation from xylene, had m. p. 154° and was identical with the dione (XII). Fraction (*b*) on acid hydrolysis gave 5-cyclo*pentane*spirodicyclo*pentan*-4-*ol*-3-*one*-1-*carboxylic acid* (5-cyclo*pentane*spirocyclo*penten*-4-*ol*-3-*one*-1-*carboxylic acid*, XIV), which crystallised from xylene in needles, m. p. 110° (decomp.) (Found: C, 61·2; H, 5·9. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%).

(B) *Oxidation of* 5-cyclo*Pentane*spirodicyclo*penten*-3-*ol*-1 : 2-*di-carboxylic Acid* (5-cyclo*Pentane*spirocyclo*pentadien*-3-*ol*-1 : 2-*di-carboxylic Acid*) (VIII, IX) *with Potassium Ferricyanide.*—A solution of the dibasic acid (1 g.), potassium ferricyanide (20 g.), and potassium carbonate (20 g.) in 80 c.c. of water was kept for 256 hours at 60°. The cooled product was acidified with hydrochloric acid, and ether then extracted a substance which solidified on prolonged desiccation; after recrystallisation from xylene, this had m. p. 154° and was identical with the dione (XII) described above. No other substances could be detected.

(C) *Oxidation of* 5-cyclo*Pentane*spirodicyclo*pentan*-3-*one*-1-*carb-oxylic Acid* (5-cyclo*Pentane*spirocyclo*penten*-3-*one*-1-*carboxylic Acid*) (X, XI) *with Alkaline Permanganate.*—To a solution of the monobasic acid (3 g.) and potassium carbonate (2 g.) in 50 c.c. of water, 1000 c.c. of 1% potassium permanganate solution (equiv. to 5O) were slowly added. After 12 hours, the excess of permanganate was destroyed by sulphur dioxide and the precipitated manganese oxides were filtered off and extracted with hot water. The combined filtrate and aqueous extract was partly evaporated, slightly acidified with hydrochloric acid, made just alkaline with ammonia, and treated with calcium chloride; *no oxalate was precipitated,*

The acidified liquid was extracted with ether, yielding 1·5 g. of *αα-dihydroxy*cyclo*pentane*-1 : 1-*diacetic acid* (XV), which crystallised from chloroform in prisms, m. p. 98° (Found : C, 49·7 ; H, 6·7. $C_9H_{14}O_6$ requires C, 49·6 ; H, 6·5%). This compound was converted by heating at 90° for an hour into α-keto*cyclo*pentane-1 : 1-diacetic acid (XVI), m. p. 112° after crystallisation from ligroin (compare Lanfear and Thorpe, J., 1923, **123**, 1688) (Found : C, 54·3 ; H, 5·7. Calc. : C, 54·0 ; H, 6·0%) ; which was converted by heating with *o*-phenylenediamine in glacial acetic acid into the quinoxaline, m. p. 222°, described by Lanfear and Thorpe (*loc. cit.*) (Found : C, 66·3 ; H, 6·0. Calc. : C, 66·1 ; H, 5·9%).

(D) *Oxidation of* 5-cyclo*Pentane*spirodicyclo*penten*-3-*ol*-1 : 2-*dicarboxylic Acid* (5-cyclo*Pentane*spirocyclo*pentadien*-3-*ol*-1 : 2-*dicarboxylic Acid*) (VIII, IX) *with Alkaline Permanganate*.—To a solution of the dibasic acid (1 g.) and potassium carbonate (0·7 g.) in 50 c.c. of water, 65 c.c. of 3% potassium permanganate solution (equiv. to 4O) were slowly added. After 12 hours, the excess of permanganate was destroyed by sulphur dioxide, and the alkaline solution obtained as in the case of the monobasic acid was freed from oxalate as calcium salt (0·6 g.). The acidified filtrate on extraction with ether yielded 1·2 g. of a mixture, m. p. 96—105°, of the keto- and dihydroxy-acids (XV, XVI), consisting mainly of the former (Found : C, 52·7 ; H, 6·3%). This mixture was converted into the quinoxaline, m. p. 222°, mentioned above.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant with which the expenses of this research were met, and to Professor C. K. Ingold, F.R.S., for his interest and valued suggestions during its progress.

THE UNIVERSITY, LEEDS. [*Received, March 10th*, 1928.]

CLXXIV.—*The Interaction of Benzoyl Chloride and Diazomethane together with a Discussion of the Reactions of the Diazenes.*

By WILLIAM BRADLEY and ROBERT ROBINSON.

MEYER (*Monatsh.*, 1905, **26**, 1300) and Schlotterbeck (*Ber.*, 1907, **40**, 479 ; 1909, **42**, 2559) observed that certain aldehydes react with diazomethane with formation of methyl ketones,

$$R{\cdot}CHO + CH_2N_2 \longrightarrow R{\cdot}CO{\cdot}CH_3 + N_2,$$

and Clibbens and Nierenstein (J., 1915, **107**, 1491) stated that an

analogous reaction occurred to a predominating extent when certain acid chlorides were employed:

$$R{\cdot}COCl + CH_2N_2 \longrightarrow R{\cdot}CO{\cdot}CH_2Cl + N_2.$$

Subsequently Nierenstein and his co-workers greatly extended the scope of the reaction and favourable yields were said to be obtained in many cases (Nierenstein, J., 1920, **117**, 1153; Nierenstein, Wang, and Warr, *J. Amer. Chem. Soc.*, 1924, **46**, 2554; Kahil and Nierenstein, *ibid.*, p. 2557; Lewis, Nierenstein, and Rich, *ibid.*, 1925, **47**, 1728; Dale and Nierenstein, *Ber.*, 1927, **60**, 1026). This reaction of diazomethane has received very little attention from other workers, but a footnote in a paper by Staudinger and Mächling (*Ber.*, 1916, **49**, 1973) records the fact that only very small yields of αα′-dichloro- and αα′-dibromo-diacetyl were obtained from oxalyl chloride and bromide respectively by the action of diazomethane and the major products could not be purified or were not examined; the work is attributed to Dr. H. Schlubach.

In the course of some synthetical experiments we wished to make an application of Nierenstein's reaction, but in the rather complex case studied an excellent yield of a diazo-ketone was obtained and this served our purpose even better than a chloroketone would have done. We therefore turned to the typical case of benzoyl chloride and diazomethane and found exactly the same results, namely, the formation of diazoacetophenone in high yield:

$$Ph{\cdot}COCl + 2CH_2N_2 \longrightarrow Ph{\cdot}CO{\cdot}CHN_2 + CH_3Cl + N_2.$$

Clibbens and Nierenstein (*loc. cit.*) stated that benzoyl chloride (1 mol.) and diazomethane (1 mol.) gave a product from which a 72% yield of ω-chloroacetophenone was isolated by distillation. Under these conditions we think the residue after removal of the solvent would consist of diazoacetophenone (0·5 mol.) and benzoyl chloride (0·5 mol.) and if this mixture were distilled, especially in presence of water, it might give some ω-chloroacetophenone. In later work Nierenstein used diazomethane in excess, sometimes in great excess, and under these conditions the formation of the chloro-ketone would be minimal. It is well known that acids decompose diazomethane very much more rapidly than they decompose diazoacetophenone—we have confirmed this observation, working with hydrogen chloride in ethereal solution. In our experiments the recognition of traces of ω-chloroacetophenone in the actual reaction mixture was facilitated by the powerful lachrymatory properties and characteristic odour of the compound; it was not isolated in substance from the mother-liquors of the diazoacetophenone.

The formation of diazoacetophenone in this manner does not constitute a novel type of reaction, for Staudinger and Mächling (*loc. cit.*) and Staudinger, Becker, and Hirzel (*Ber.*, 1916, **49**, 1973) have shown that ethyl diazoacetate can be acylated in a similar manner and in accordance with the following example :

$$COCl_2 + 2CHN_2{\cdot}CO_2Et \longrightarrow COCl{\cdot}CN_2{\cdot}CO_2Et + CH_2Cl{\cdot}CO_2Et + N_2.$$

On the other hand, diphenyldiazomethane was found by Staudinger, Anthes, and Pfenninger (*Ber.*, 1916, **49**, 1941) to be inactive towards benzoyl chloride and to react with carbonyl chloride and oxalyl chloride in accordance with the scheme :

$$CPh_2N_2 + COCl_2 \longrightarrow CPh_2Cl{\cdot}COCl + N_2.$$
$$CPh_2N_2 + COCl{\cdot}COCl \longrightarrow CPh_2Cl{\cdot}CO{\cdot}COCl + N_2.$$

In these cases it is obvious that the formation of a diazo-ketone is not feasible.

Lewis, Nierenstein, and Rich (*loc. cit.*) state that benzoyl bromide, treated with diazomethane, gives rise to ω-bromoacetophenone in 28% yield and 3 : 6-dibromo-3 : 6-diphenyl-1 : 4-dioxan in 62% yield. The chemistry involved in the degradation of the latter substance is of an unconventional type. The dibromodiphenyldioxan contains two CPhBr·O· groups, yet it is stable and crystallises from alcohol unchanged. It may be redneed by treatment with activated magnesium in dry ether and decomposition of the product (yield, 76%); the resulting 3 : 6-diphenyl-1 : 4-dioxan, a diphenyl derivative of ethylene ether, may then be hydrolysed to phenylethylene glycol, $CHPh(OH){\cdot}CH_2{\cdot}OH$, in 3 hours by means of 10% aqueous potassium hydroxide on the steam-bath and in presence of benzene (yield, 62%). In our experiments benzoyl bromide and diazomethane yielded diazoacetophenone.

Mechanism of the Reactions of the Aliphatic Diazo-compounds.—On the basis of the electronic theory of valency the Angeli–Thiele formula for the diazenes becomes $CR_2{=}\overset{+}{N}{=}\overset{-}{N}{=}$ (each line representing two electrons), and we may assume that the driving force in the manifold reactions of these substances is the tendency to neutralise the charges associated with the nitrogen atoms.

An examination of these reactions reveals two striking and apparently anomalous circumstances. In the first place diazomethane, this example being used for convenience, is both anionoid and kationoid; it reacts vigorously with electron-seeking agents, for example, protons and halogen molecules, and with electron-donating agents, for example, organo-metallic compounds. It is true that different positions in the diazomethane molecule are involved, but the second apparent anomaly is that the carbon atom

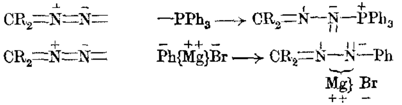
next to the positively charged nitrogen is the anionoid centre and the negatively charged nitrogen is the kationoid centre.

The indication is that the *maintenance of atomic electron configurations* is a far more urgent need than the neutralisation of charges and that in both cases, paradoxical though it seems at first sight, the electronic changes do ultimately lead to a more even distribution of the charge. The conjugative electron displacements which we postulate are represented in the annexed figures.

Anionoid reactivity at C. *Kationoid reactivity at terminal N.*

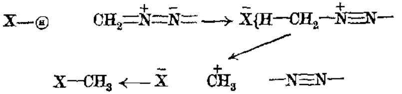
In (A) the charge on the central nitrogen remains unchanged but that on the terminal nitrogen is transferred in part to carbon. In (B) the charge on the central nitrogen is neutralised, but of course the terminal nitrogen receives electrons from outside and some other atom must acquire a positive charge.

Two simple examples of the operation of scheme B are the following:



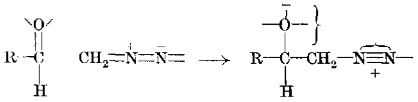
Behaviour towards cyanidion is regarded as one of the most searching tests for kationoid reactivity, and not only $\overline{CN}$ but also $\overline{SO_3Na}$ attach themselves to the terminal nitrogen atom of the diazenes.

In the action of acids on the diazenes we probably see scheme (A) at work, because the stronger acids, HX, in which the free electrons of X are least active, react most easily with the diazo-compounds.

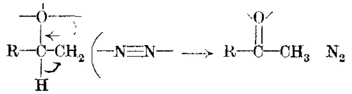


Here we assume the intermediate formation of a diazonium salt and a final decomposition along familiar lines. The reaction with the halogens is entirely analogous and may be summarised by the expressions: $Br_2 + CH_2N_2 \longrightarrow Br{\cdot}CH_2{\cdot}\overset{+}{N_2}\}\overline{Br} \longrightarrow Br_2CH_2 + N_2$.

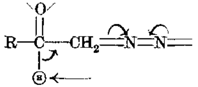
Schlotterbeck's reaction presents a more complex case :



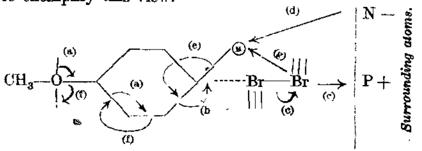
and



Such recoil reactions are common in this group, but it is not necessary to assume a completed transfer of a charge as in the above representation. The first phase of the process may well proceed to a fractional extent only and once the carbon atoms are connected the main changes leading to the separation of nitrogen and the wandering of a proton will proceed by a more direct route as in the expression

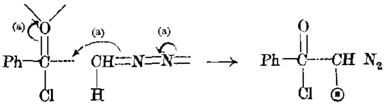


This conception of a reaction oriented or directed by a process involving fractional valencies and then carried to completion by a different and more direct mechanism was first suggested by one of us in 1920 (Robinson, *Mem. Manchester Phil. Soc.*, **54**, No. 4) and stated to be applicable to *m*-substitutions in benzene derivatives. Ingold and Ingold have since put forward a similar scheme in connexion with *o*-*p*-substitutions also (J., 1926, 1313). An alternative hypothesis is that of vibrations of the electronic displacements (Robinson, B.A. Meeting, Southampton, 1925; *Chem. News*, 1926, **133**, 7). These may be rapid and of quite small amplitude and the substitution processes and other reactions would then be approximately continuous. The bromination of anisole may be used to exemplify this view.

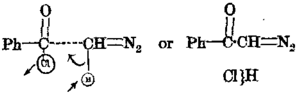


The substitution is supposed to be initiated by the tendency of bromine to acquire electrons. This can be satisfied in the *o-p*-positions (not in *m*-) and a bond is produced by the displacement (b) because the consequent displacements (a) are possible owing to the fact that the oxygen atom affords a resting place for the positive charge, where it is balanced by the surroundings (N). The partial formation of the C—Br bond (b) enables the second bromine atom to consummate to the same fractional extent (c) its tendency to become bromidion when it is electrovalently associated with surroundings (P). A circuit is thus completed and the movement of electrons in it has involved a tentative attachment of bromine to carbon and an equal separation of bromidion. The oxygen atom is not, however, in its most stable condition and reverts to this by an electron displacement (electrical current) in a different circuit, this time involving the hydrogen atom and not affecting (b) or (c). The lines of force between (N) and the oxygen atom are broken; then (f) reverses (a) and (e) and (d) are consequences. The partly liberated proton may seek the centres (N) or there may be any degree of short-circuiting up to the limit expressed by (g), which is an alternative or part alternative to (d). The first-mentioned set of displacements and processes (a), (b), (c) can then occur again and alternate with the recovery displacements (d), (e), (f) until the substitution is completed. It is possible to construct similar schemes for other reactions involving conjugated systems of various types.

We represent the formation of diazoacetophenone in the following manner :



At this stage the terminal nitrogen has succeeded in transferring a fraction of its negative charge to the oxygen atom and a bond between the carbon atoms has been initiated. The repulsion exerted by the central nitrogen on the proton indicated is now reinforced by that exerted by the oxygen and chlorine nuclei and the following changes may be almost synchronous :

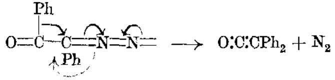


The initial electronic changes (a) may be to some extent permanent, since the oxygen atom can well hold a part of the negative charge, or, naturally, the strain may be completely or partly released by reversal of these displacements.

The reactions of the diazenes with unsaturated ethenoid substances seem to belong to both types (A) and (B) and in either case the mode of occurrence of these additive processes can be readily accommodated by the electronic theory. There is need of further work on the constitution of the primary additive products of aliphatic diazo-compounds and unsymmetrical unsaturated substances.

In the polymerisation of the diazo-compounds, for example, the formation of pseudodiazoacetic acid, the kationoid centre of one molecule evidently attacks the anionoid centre of another.

Finally the varied decompositions are readily interpreted, one of the most interesting being that discovered by Schröter (*Ber.*, 1909, **42**, 2346) :



EXPERIMENTAL.

Materials.—Diazomethane was prepared from nitrosomethylur ethane and its ethereal solution was slowly distilled through a 45 cm column. The volume of nitrosomethylurethane required wa calculated from the normal yield under standard condition (Houben-Weyl, "Die Methoden der Organischen Chemie," 1923 **3**, 124), that is, 0·18—0·20 g. of diazomethane from 1 c.c. of nitroso methylurethane.

Ether was dried over phosphoric oxide and distilled through th apparatus immediately before an experiment.

A fresh specimen of benzoyl chloride from Kahlbaum wa employed.

Diazoacetophenone.—(A). A solution of benzoyl chloride (2·5 g. 1 mol.) in ether (5 c.c.) was added to an ethereal solution of diazo methane (1·25 mols.) maintained at $-5°$ to $0°$. A mild evolution of nitrogen occurred and continued for 1—$1\frac{1}{2}$ hours. The yellow solution was kept over-night, and the ether then evaporated in a rapid current of air. The residue consisted of a colourless oi (1·0—1·5 g.), easily soluble in 10 c.c. of cold light petroleum, togethe with a pale yellow, crystalline material (1·3 g.) which on recrystal lisation from light petroleum afforded diazoacetophenone (1·10 g.) m. p. 47—49°.

(*B*). The above experiment was repeated with the addition o

tripropylamine (2·5 g.) and the result was a product containing unchanged benzoyl chloride, tripropylamine, a trace of ω-chloroacetophenone (recognised by odour only), and diazoacetophenone (1·2 g.). Evidently the tertiary base does not effectively de-activate the liberated hydrogen chloride.

(C). Benzoyl chloride (2·1 g.; 1 mol.) was treated as in (A) with diazomethane (2 mols.). After 24 hours the ether was evaporated, leaving a crystalline residue, which was washed with light petroleum (25 c.c.) and then weighed 1·8 g. The light petroleum deposited a further 0·05 g. of the substance and on evaporation left about 0·1 g. of a yellow oil containing benzoyl chloride, diazoacetophenone, and a mere trace of ω-chloroacetophenone (odour). The yield in this experiment amounted to 91% of that theoretically possible.

The solid products described above as consisting of diazoacetophenone exhibited identical behaviour and were free from ω-chloroacetophenone. The substance crystallised from light petroleum in pale yellow, flat needles, m. p. 48—48·5° (Wolff, *Annalen*, 1903, **326**, 142, gives m. p. 49—50°) (Found: C, 65·9; H, 4·1. Calc. for $C_8H_6ON_2$: C, 65·7; H, 4·1%).

The substance decomposed in contact with porous material at 116—118°. An alcoholic solution was coloured deep red on the addition of sodium hydroxide or alternatively by the addition of zinc dust and ammonia became purple or blue according to the conditions (Wolff, *Annalen*, 1902, **325**, 141).

The substance exhibited the characteristic reactions of an aliphatic diazo-compound. Iodine decomposed it instantly in cold alcoholic solution with evolution of nitrogen, and the action of dilute sulphuric acid gave nitrogen and a substance (benzoylcarbinol) that quickly reduced Fehling's solution in the cold.

Quantitative and smooth decomposition occurred on warming with glacial acetic acid. The product was isolated by means of ether and crystallised from light petroleum in large, colourless tablets, m. p. 48—49° (Zincke, *Annalen*, 1883, **216**, 308, gives m. p. 49—49·5°). The substance reduced Fehling's solution in the cold in the course of ½—1 minute and its m. p. was not depressed by admixture with an authentic specimen of ω-acetoxyacetophenone.

The formation of methyl chloride in the reaction between benzoyl chloride (1 mol.) and diazomethane (2 mols.) was not experimentally confirmed.

Interaction of Benzoyl Bromide and Diazomethane.—Benzoyl bromide (2·8 g.; 1 mol.) in ether (5 c.c.) was added to an ethereal solution of diazomethane (2 mols.) at − 5° to 0°. The vigorous evolution of nitrogen, appeared to be complete in 5—10 minutes, but

the mixture was kept over-night. The semi-solid residue after removal of the ether was dissolved in boiling light petroleum and, on cooling, diazoacetophenone (1·25 g.), m. p. 45—47°, separated. A further quantity (0·4 g.), m. p. 44—46°, was obtained from the mother-liquor. The main fraction mixed with pure diazoacetophenone had m. p. 46—48°; on recrystallisation from light petroleum it was obtained in long, flat, pale yellow needles, m. p. 48—49°, exhibiting the characteristic reactions. The final mother-liquor contained benzoyl bromide and, apparently, a trace of ω-bromoacetophenone.

THE UNIVERSITY, MANCHESTER. [*Received, March 22nd, 1928.*]

CLXXV.—*The Hypothesis of Valency-deflexion.*

By CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE.

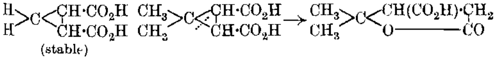
IN a recent issue of the *Fortschritte der Chemie, Physik und physikalischen Chemie* (Bd. **19**, Heft. 4, 1927) Hückel discusses our view that the disparity between the space-requirements of the several groups attached to a central carbon atom modifies the angle between the valencies of that atom. The discussion includes a partial statement of experimental data which have been interpreted by ourselves and others in the light of the hypothesis mentioned, and a criticism which, since it reveals lack of understanding of the essentials of the hypothesis, will briefly be considered here.

In the first place, it must be remarked that the calculations of the angles between the valencies of an atom from molecular volume data have never been regarded by us as otherwise than illustrative of the qualitative implications of the theory, and of the manner in which it might be developed when the constitution of the combined carbon atom is more fully worked out. The theory is, in fact, intended to be translated as our knowledge of the constitution of the atom grows, and it therefore need scarcely be said that the assumption of distorted valencies does not imply, as Hückel asserts, that the forces of valency are assumed to be of gravitational type governed by the law m_1m_2/r^2. The details of this, the principal subject of Hückel's criticism, require no further comment.

Hückel's further criticism regarding the applications (which he regards as arbitrary) of the hypothesis fails for two reasons. In the first place, whilst we have consistently endeavoured to restrict the applications of the hypothesis to cases which are comparable in the sense that polar disturbances are at a minimum, Hückel endeavours to extend the comparisons on the same pure

patial basis to examples in which polar influences would be expected o act powerfully and very differently, and, in commenting on the ecognition of the necessity for taking count of polar influences, sks "Wozu diese ad hoc gemacht Annahme?" We are not ware that the existence of polar influences in Organic Chemistry ias previously been disputed, and it is certainly true that modern vork has yielded much definite information with regard to them. 'wo examples may be given to illustrate the difference between our omparisons and those of Hückel. The ease of formation of a series of *cyclo*propanedicarboxylic acids from glutaric acids by mono- rromination and subsequent hydrolysis under comparable con- litions,

ias been shown to follow the anticipated order (for example, glutaric acid 47%, ββ-dimethylglutaric acid 84% of ring-formation). This comparison is a just one, for the β-alkyl groups would be expected to have only second-order polar effects on the α-hydrogen and α-bromine, and the possibility that polar disturbances might affect the result is still further diminished by the circumstance hat they will be of opposite sign for the two atoms indicated. Hückel, however, seeks to produce a parallel case pointing in the opposite direction by comparing the stability of *cyclo*propane-1 : 2-dicarboxylic acid with the tendency of the 3 : 3-dimethyl derivative to yield terebic acid :



(stable)

In our view this comparison is unjust, because the first-order polar effect of the methyl groups would be in the direction of increasing the vulnerability of the quaternary carbon atom in the reaction considered, and this might be expected to outweigh the spatial influences. Again, Hückel considers the evidence to be derived from the dissociation constants of the alkylmalonic acids, and points out that the results do not fall into the regular sequence which might be expected if the spatial hypothesis advanced by us were the only factor in the situation. This, however, need not occasion surprise; but it is to be noted that Hückel does not attempt a corresponding analysis of the data relating to the β-alkylated glutaric acids in which the polar effect of the alkyl groups would be expected to be diminished (see Spiers and Thorpe, J., 1925, **127**, 538). Even this series would not be expected to conform *exactly* to the requirements of our hypothesis, but it should certainly con-

form much more closely than the series of malonic acids; and although the available data for the second dissociation constants (which are required for the application of the Bjerrum calculation) are rather few, there is already evidence that the anticipated closer conformity exists, and we confidently expect that further measurements will substantiate this conclusion. It must be confessed that many examples exist in which it is impossible in the present state of knowledge to foretell the effect of polar influences on the angular relations of the valencies—for instance, in the Dieckmann-Komppa synthesis of *cyclo*pentanedionedicarboxylic esters, ir which a concentration of highly polar groups is produced. In these circumstances, we do not pretend to be able to foretell the conditions of substitution which will produce the system having greates stability. In such examples, the examination of the effect of serie of substituents of increasing bulk often reveals a maximum o stability at some intermediate member, with falling-off in botl directions. There is, however, nothing in this behaviour which i demonstrably inconsistent with the theory (as Hückel asserts) although it must be admitted that the full explanation cannot ye be given.

The remaining point relates to the theory of the strainless form of the 6- and 7-membered rings. Hückel's contention is expresse in the assertion that our hypothesis "steht und fällt mit der wil kürlich Annahme eines ebenen gespannten Sechsrings." It is tru that in our first memoir (J., 1915, **107**, 1080) the *cyclo*hexane rin was assumed to be uniplanar; but the whole application of th valency distortion hypothesis to 6- and higher-membered rings wa modified in 1923 (Baker and Ingold, J., **123**, 122) contemporar eously with, and independently of, the publication by Hückel ar others of the first experimental evidence relating to the existen of isomerides of the decahydronaphthalene type. This explic modification, ignored by Hückel, may be restated as follows. Th intrinsically probable existence of strainless multiplanar forr (Sachse, 1890; Mohr, 1918) of the *cyclo*hexane ring, combined wi the non-existence of isomerides which should arise if such forr were static, leads to the suggestion that these forms (*cis* and *tra* are to be regarded as limiting states of a vibrating framework, t average condition of which is between the uniplanar and strainl condition. (The occurrence of isomeric decahydronaphthalenes which each ring "locks" the other merely proves that the mul planar forms *can exist*, not that they represent a permanent co dition in the absence of locking.) It was a natural corollary tl the further a uniplanar form departed from the strainless conditi as, for example, in 7- and 8-membered rings, the more would t

average condition recede from the uniplanar state. This view, which was subsequently emphasised by Baker and others, is in excellent agreement with the available data, and Hückel's statement quoted above is thus seen to be unwarranted.

In justice to the views discussed by Hückel, it should be remarked that this memoir contains no constructive suggestion as to any alternative to the hypothesis on the basis of which we have consistently endeavoured to collate a large body of data; yet observations continue to accumulate which obviously require interpretation. Reference may be made to Vogel's recent demonstration (*J.*, 1927, 594) that, whereas $\alpha\delta$-diacetylbutane exists in the open-chain form, its $\beta\beta\gamma\gamma$-tetramethyl derivative reacts in the cyclol form only :

$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \\ | \\ CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 \end{array} \qquad \begin{array}{l} CMe_2{\cdot}CH_2{\cdot}C(OH){\cdot}CH_3 \\ | \\ CMe_2{\cdot}CH{\cdot}CO{\cdot}CH_3 \end{array}$$

and to Rothstein and Shoppee's elaboration (*ibid.*, p. 531) of the earlier observations of one of us relating to the progression and substitution of the stability of the lactolone forms of the α-ketoglutaric acids :

$$\begin{array}{l} CH_2{\cdot}CO{\cdot}OH \\ | \\ CMe_2{\cdot}CO{\cdot}CO_2H \\ \quad\text{(stable)} \end{array} \qquad \begin{array}{l} CHMe{\cdot}CO{\cdot}OH \\ | \\ CMe_2{\cdot}CO{\cdot}CO_2H \end{array} \rightleftharpoons \begin{array}{l} CHMe{\cdot}CO{\cdot}O \\ | \\ CMe_2{\cdot}C(OH){\cdot}CO_2H \end{array}$$

(balanced system)

$$\begin{array}{l} CMe_2{\cdot}CO{\cdot}O \\ | \\ CMe_2{\cdot}C(OH){\cdot}CO_2H \\ \quad\text{(stable)} \end{array}$$

The facts which have been accumulated during the past 13 years are now so numerous that the hypothesis by which we have endeavoured to collate them cannot lightly be brushed aside unless some alternative view can be advanced. Some of the points dealt with in this communication were raised also by Sidgwick in his work "The Electronic Theory of Valency," Oxford, Clarendon Press, 1927.

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THE UNIVERSITY, LEEDS.

[*Received, March 3rd*, 1928.]

CLXXVI.—*Experiments on Transmutation.*

By JOHN ALBERT NEWTON FRIEND.

IN 1907 Ramsay (*Nature*, 1907, **76**, 269; Ramsay and Cameron, J., 1907, **91**, 1606; Ramsay, J., 1909, **95**, 624) observed the presence of spectroscopic amounts of lithium in solutions of copper nitrate

and sulphate after exposure to radium, whereas parallel experiments with lead nitrate solution did not lead to any conclusive result. Ramsay suggested that the copper had been transmuted to the lowest member of its series, *i.e.*, lithium, although the possibility was not excluded that the chief product in the degradation of copper was sodium.

Repetition of the experiments by Curie and Gleditsch (*Compt. rend.*, 1908, **147**, 345; see also Ramsay and Cameron, *ibid.*, 1908, **146**, 456), in which containing vessels of platinum instead of glass were employed, failed to yield a similar result and the authors concluded that Ramsay's results were due to dissolution of lithium already present in the glass of his apparatus. Perman (J., 1908, **93**, 1775) exposed solid copper sulphate and nitrate, a solution of gold chloride, and some precipitated gold to the action of radium bromide for several months, but obtained no evidence of transmutation to lithium.

These experiments do not definitely disprove Ramsay's theory, but they certainly offer no support. In more recent experiments, attention has in the main been directed to methods involving electronic bombardment only, although Rutherford (*Proc. Roy. Soc.*, 1920, *A*, **97**, 374; J., 1922, **121**, 400; *Brit. Assoc. Rep.*, 1923, 16), employing an exceedingly delicate physical method, has proved that rapidly moving α-particles are capable of effecting the disruption of stable atoms.

It seemed desirable, therefore, that further experiments on the effect of exposure to radium "rays" should be carried out, and the spectra of the exposed substances examined over their whole range, and not merely for the presence of lithium.

Experimental.

Expt. 1. A small flat crystal of pure barium sulphate was exposed in air to bombardment for 3 years from a feeble source of radium-*D*, -*E*, and -*F*. The optical spark spectrum was photographed by Messrs. Adam Hilger, but no lines appeared that did not also appear on the blank.*

Expt. 2. A crystal of barium sulphate, a small piece of pure silver foil, and one of pure gold foil (A) were laid horizontally in a glass tube separated by pure cotton wool. The tube was evacuated and, at intervals, varying quantities of emanation were admitted, *viz.*, 28 millicuries at the first filling on Dec. 20th, 1926, and 32, 20, and 23 millicuries, respectively, at intervals of 5 or 6 weeks. The

* Condensed spark spectra both with and without the introduction of a Hemsalech coil into the circuit.

spark spectra of the barium sulphate and silver coincided exactly with those of the blanks, but the gold spectrum showed calcium lines λ 3934, 3968, not present in the blank, and stronger copper lines than occurred in the blank, λ 3274 and 3247.

Expt. 3. As the glass containing-tube had been strongly discoloured, it appeared possible that the calcium found in the gold had come from this source, although in that event one might have expected to find traces in the silver and barium sulphate, which was not the case.

The experiment was therefore repeated with fresh pieces from the same sheet of gold foil (A), and with foil obtained from a different source (B). The specimens were laid in a silica test-tube enclosed in a wider glass tube, no cotton wool being employed. The glass tube was drawn out, evacuated and finally sealed after admission of 250 millicuries of emanation.

After 2 months the specimens were removed and dispatched with blanks to Professor A. Fowler, who had generously consented to examine their spectra. Calcium lines * appeared, not only in both exposed specimens, but also in both blanks. They were short, confined to the region near the poles, and of low intensity. In specimen A the lines appeared to be stronger in the exposed sample than in the unexposed, but the reverse was the case with specimen B.

It would appear, therefore, that the lines in both Expts. 2 and 3 were due to traces of calcium present in the original specimens, though somewhat irregularly distributed. If any kind of transmutation had taken place, its quantity was too minute to admit of detection spectroscopically

The silica tube used in Expt. 3 assumed a uniform violet-purple colour. This agrees with the statement by Lawson (*Nature*, 1919, **104**, 335) that the silica vessels used by Hönigschmid in his researches on the atomic weight of radium became dark violet, although in this case the colouring was streaky. In Doelter's experiments (quoted by Clarke, *Trans. Soc. Glass. Tech.*, 1921, **5**, 155) pure quartz was coloured uniformly brownish-red by radium salts, and Clarke appears to regard brown as the normal coloration for quartz. Unfortunately, neither author gives the wave-lengths of the transmitted light, and verbal descriptions of colour effects may be misleading. The silica used in the tests here described showed absorption at both the red and the violet end of the spectrum. Absorption did not begin sharply, but gradually increased in intensity with the distance from the middle of the visible spectrum. Speaking generally, light of λ 5000 to 7000 Å.U. was transmitted quite well, the remainder of the spectrum being comparatively feeble.

* Spark spectra, with inductance. Lines of λ 3934 and 3968 Å.U.

In conclusion, the author desires to thank Professor Fowler for examining the spectra of the gold specimens used in Expt. 3, and the Radium Institute for assistance in exposing the specimens in Expts. 2 and 3.

THE TECHNICAL COLLEGE, BIRMINGHAM. [*Received, April 18th,* 1928.]

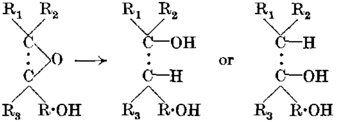
CLXXVII.—*Constituents of* Myoporum lætum, *Forst. (The "Ngaio"). Part III. The Oxide Rings of Ngaione.*

By FREDERICK HENRY McDOWALL.

THE experiments on ngaione now to be described (see also J., 1925, **127**, 2200; 1927, 731) were carried out for the most part as a preliminary to a more exhaustive investigation of the oxide rings present in the molecule. As, however, the work has been interrupted, the results are published in their present incomplete form.

From the stability of ngaiol to water under pressure (see later), and of ngaiol and tetrahydrongaiol to acetic anhydride (*loc. cit.*), it is concluded that an ethylene oxide ring is not present in the molecule. Some ethylene oxide rings, however, show extraordinary stability, especially in dioxidic compounds. Pinol oxide, *e.g.*, is more stable than most ethylene oxides, and furyl butylene oxide (Tonnies and Staub, *Ber.*, 1884, **17**, 854) is not affected by acetic anhydride (compare also the naturally occurring diethylene oxide of linalol; and mannitol anhydride, which does not combine with water at all).

The fission of an oxide ring in ngaiol by hydrogenation has already been recorded (*loc. cit.*, 1927). By means of hydrogen and platinum-black in glacial acetic acid a different *glycol* is obtained, possibly through fission of a different oxide ring, or alternatively through fission of different oxygen bonds of the same oxide ring:



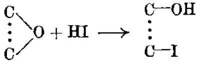
The glycols differ in their physical properties and in their colour reactions with vanillin and concentrated hydrochloric acid.

The action of halogen acids on some hydrogenated derivatives of ngaione has been studied. Tetrahydrongaiene dioxide, when treated with hydrogen chloride in glacial acetic acid solution,

gave what is probably a monochloro-oxido-acetate. Tetrahydrongaiol was converted by hydrogen iodide in glacial acetic acid into a polyiodo-acetate, from which a mixture of unsaturated monohydric alcohols was obtained by reduction and saponification. From the mixture of products an alcohol, $C_{15}H_{29}$·OH, was isolated, and in one instance an ethylene glycol, $C_{15}H_{30}(OH)_2$. Unsuccessful attempts were made to reduce the iodo-acetates without the formation of ethylenic linkings. Hydrogen with palladinised barium sulphate alone had no reducing effect, and addition of alkali caused elimination of hydrogen iodide with formation of several ethylenic linkings, and possibly an oxide ring. Reduction with zinc dust and glacial acetic acid, saturated with hydrogen iodide at 0°, yielded an iodine-containing product which after further reduction with zinc dust and alcohol was again unsaturated. Reduction with zinc dust and glacial acetic acid, saturated with hydrogen iodide at −10°, followed by reduction with zinc dust and alcohol and then by hydrogenation with platinum-black in glacial acetic acid, yielded a mixture of alcohols from which, after saponification, a paraffin alcohol, or mixture of paraffin alcohols, $C_{15}H_{31}$·OH, was isolated. The isolation of this paraffin alcohol and of the ethylene glycol (see above) establishes beyond all doubt the conclusion (*loc. cit.*, 1927) that the molecule of ngaione is free from carbocyclic rings. Tetrahydrongaione gave on treatment with hydrogen iodide and glacial acetic acid an oily polyiodoketo-acetate, which by reduction and saponification was converted into a mixture of keto-alcohols.

Reduction of tetrahydrongaiol with red phosphorus and constant-boiling hydriodic acid under reflux gave an oily di-iodide, which on further treatment with zinc dust and alcohol yielded a mixture of an alcohol with an unsaturated or cyclic hydrocarbon.

The formation of a monoacetate from tetrahydrongaiol suggested that the secondary alcoholic group had become esterified by the acetic acid in the presence of the hydrogen iodide, and had thus escaped reduction. A consideration of all the results indicates, however, that the problem is more complex. The formation of an acetate from tetrahydrongaiene dioxide by the action of hydrogen chloride in glacial acetic acid, the complexity of the mixture of monohydric alcohols obtained in the experiments with tetrahydrongaiol, and the formation of keto-alcohols from tetrahydrongaione all show that opening of one of the oxide rings can take place according to the equation



The alcoholic group is probably simultaneously esterified. The original secondary alcoholic group of tetrahydrongaiol is thus probably removed by conversion into the iodide and subsequent reduction.

The evidence accumulated does not permit any far-reaching speculation on the formula of ngaione. No certain indications of the absence of a furan ring have been obtained. Ngaione and ngaiol give violet colours in the pine-shaving test (compare furan and furfural, which give green colours). One would also expect a furan derivative to be rather more unstable than ngaione. On the other hand the molecular refractions of ngaione, ngaiol, and their derivatives show depressions of the order of that (average, 0·44) shown by furan derivatives (Wienhaus, *Ber.*, 1920, **53**, 1660). As with the furan compounds, the depression almost disappears on hydrogenation (*loc. cit.*, 1927). The values for the molecular refraction seem definitely to exclude the possibility of a furyl-ketone grouping of the type prepared synthetically by Asahina and Murayama (*Arch. Pharm.*, 1914, **252**, 435), $C_4OH_3\cdot COR$, which showed a large exaltation (average, approx. 1·0).

The tendency to formation of enolic acetates shown by ngaione (*loc. cit.*, 1925) is unusual for a ketone, and suggests that an esocyclic keto-oxide may be present of the type prepared by Dupont (*Compt. rend.*, 1911, **152**, 1486; **153**, 275; *Ann. Chim.*, 1913, **30**, 485), $O<\begin{matrix}CMe_2\cdot CH_2\\ CMe_2\cdot CO\end{matrix}$, which shows the reactions of the carbonyl group and a tendency to enolisation. The analogy can, however, only be regarded as tentative, as the properties of esocyclic keto-oxides are not well known (compare ketocineole, Cusmano and Linari, *Gazzetta*, 1912, **42**, i, 1, and the tetrahydro-γ-pyrones, Borsche and Thiele, *Ber.*, 1915, **48**, 684; 1923, **56**, 2012).

It has been shown that the vanillin–hydrochloric acid colour reaction is given by nearly all substances containing oxidic oxygen, but it is not confined to these substances.

A small quantity of an isomeride of ngaiol has been isolated, and also a monoxide, $C_{15}H_{24}O$.

EXPERIMENTAL.

Treatment of Ngaiol with Water.—No change in the physical constants was observed after ngaiol (1 part) had been heated for 10 hours with water (4 parts) in an atmosphere of carbon dioxide at 250°.

Hydrogenation of Ngaiol with Platinum-black as Catalyst.—Ngaiol (9·7 g.) in presence of platinum-black (1·1 g.; prepared by Feulgen's method; *Ber.*, 1921, **54**, 360) and 30 c.c. of glacial acetic

acid absorbed 3 mols. of hydrogen during 2 hours. The resulting oil was hydrolysed with alcoholic potash, and the product isolated by means of ether. A portion of the product lost water when distilled at 0·5 mm. pressure : the distillate, b. p. 160—180°/0·5 mm., was a colourless oil with a strong sweet odour, n_D^{20} 1·4707, d_{20}^{20} 0·9312 (Found : C, 73·4, 73·1 ; H, 11·9, 12·0. $C_{15}H_{30}O_3$ requires C, 69·7 ; H, 11·7%. $C_{15}H_{28}O_2$ requires C, 75·0 ; H, 11·7%) ; the saponification value of the acetate was 265.

The undistilled portion of the product of hydrogenation, after being freed from solvent in a vacuum at 100° (2 hours), was obtained as a slightly yellow, odourless oil, more viscous than the distillate described above. It had d_{20}^{20} 0·966 and n_D^{20} 1·4664, whence $[R_L]_D$ = 74·03 [calc. for $C_{15}H_{28}O(OH)_2$, 73·96] (Found : C, 69·6 ; H, 11·9. $C_{15}H_{30}O_3$ requires C, 69·7 ; H, 11·7%). When treated with vanillin and concentrated hydrochloric acid, the substance slowly developed a jade-green colour. The acetate was prepared in the usual way ; saponification value, 308 [calc. for $C_{15}H_{28}O(OAc)_2$, 326].

The direct product of hydrogenation of ngaiol under the above conditions is therefore an *oxido-glycol*, $C_{15}H_{28}O(OH)_2$, different from the glycol of the same formula obtained by hydrogenation with Skita's reagent (*loc. cit.*, 1927).

Action of Hydrogen Chloride on Tetrahydrongaiene Dioxide.—A solution of the dioxide (1·1 g.) in glacial acetic acid (10 g.) was saturated with hydrogen chloride at 0° and kept in the dark for 3 days. Dilution with water then precipitated an oil, which was extracted with ether, well washed with water and with weak sodium bicarbonate solution, and dried ; removal of the solvent at 40° and finally in a vacuum over sulphuric acid left a dark, fluid oil, which did not crystallise at −20° (Found : Cl, 10·2. $C_{15}H_{28}OCl{\cdot}OAc$ requires Cl, 11·1%). The chlorine was almost completely removed by successive treatments with zinc dust and 80% alcohol, and with zinc dust and acetic acid at 100°. The resulting oil on distillation at 29 mm. pressure gave three fractions, b. p. 185—197°, 197—213°, 213—, respectively (Found for first two fractions : C, 72·1, 71·4 ; H, 11·4, 11·3. Calc. for $C_{15}H_{29}O{\cdot}OAc$: C, 71·8 ; H, 11·4%). The saponification value of the first fraction was 200 (calc. for $C_{15}H_{29}O{\cdot}OAc$, 209). The product was therefore a mixture of acetates, formed by the opening of one oxide ring.

Action of Hydrogen Iodide on Tetrahydrongaiol.—The wine-red liquid obtained when a solution of tetrahydrongaiol (5·1 g.) in glacial acetic acid (40 g.) was saturated at 0° with hydrogen iodide became turbid after some hours, and a heavy black oil gradually separated. After 2 days, ether extracted from the mixture, diluted with water, a dark brown, unstable, uncrystallisable oil (15 g.) [Found : I, 59·6.

$C_{15}H_{27}I_4$·OAc requires I, 65·6%. $C_{15}H_{28}I_3(OAc)_3$ requires I, 59·6%. $C_{15}H_{27}OI_3$ requires I, 63·1%]. The *polyiodide* in 80% alcohol was heated with an equal weight of zinc dust on the water-bath for $1\frac{1}{2}$ hours, and ether extracted from the product a mobile brownish oil with a faint odour. On distillation at 29 mm. this gave two fractions: A_1, b. p. 168—172°, $n_D^{20°}$ 1·4442, $d_{20°}^{20°}$ 0·868; A_2, b. p. 172—, $n_D^{20°}$ 1·4488 (Found for A_1: C, 75·8; H, 12·5. $C_{15}H_{29}O$·OAc requires C, 76·0; H, 12·0%). Saponification value of A_1, 178; of A_2, 188. The liquid obtained by hydrolysis of the oil with hot alcoholic potash was isolated by means of brine and ether and divided by distillation into four fractions, all of which decolorised bromine water. Analyses indicated that the product was a mixture of unsaturated monohydric alcohols with a small quantity of hydrocarbon. The second fraction had b. p. 166—173°/29 mm., $d_{20°}^{20°}$ 0·845, $n_D^{20°}$ 1·4524, whence $[R_L]_D$ = 72·36 (calc. for $C_{15}H_{29}$·OH $|\overline{1}$: $[R_L]_D$, 72·53) (Found: C, 79·8; H, 13·8. Calc. for $C_{15}H_{29}$·OH: C, 79·6; H, 13·3%).

From the higher-boiling portion of the product of one treatment of tetrahydrongaiol with hydrogen iodide a very viscous, yellowish, odourless oil was obtained (0·55 g.), b. p. 200—215°/13 mm., $n_D^{20°}$ 1·4655, which did not crystallise during 10 hours at −10° [Found: C, 73·1; H, 13·0; *M*, by Rast's method, 248. $C_{15}H_{30}(OH)_2$ requires C, 73·7; H, 13·2%; *M*, 244. Saponification value of the acetate, 326. Calc. for $C_{15}H_{30}(OAc)_2$: S.V., 339]. The substance was thus shown to be a dihydroxypentadecane.

Reduction with palladinised barium sulphate and hydrogen. The catalyst (prepared by Schmidt's method; *Ber.*, 1919, **52**, 409) and the oily polyiodo-acetate (from 3·0 g. of tetrahydrongaiol) in absolute alcohol (30 c.c.) were stirred by means of a current of hydrogen. The reduction took place rapidly when the solution was kept slightly alkaline by frequent additions of aqueous caustic potash. After 2 hours, the solution was filtered. Extraction with ether, after addition of brine, gave an iodine-free product, from which, on hydrolysis with alcoholic potash, a light brown oil was obtained. This, on distillation at 29 mm. pressure, gave two fractions, b. p. 155—165° and 165—170°, as colourless, mobile oil with a strong aniseed odour (Found for the second fraction: C, 78·6; H, 11·8%), a third fraction, b. p. 170—180°, $d_{20°}^{20°}$ 0·904, $n_D^{20°}$ 1·4735, as a colourless oil with a sweet odour, and a fourth fraction, b. p. 180—195°, $d_{20°}^{20°}$ 0·924, $n_D^{20°}$ 1·4754, which was odourless (Found: C, 75·8; H, 11·3. $C_{15}H_{26}O$ requires C, 81·1; H, 11·7%. $C_{15}H_{26}O_2$ requires C, 74·9; H, 11·7%).

Reduction with zinc dust and glacial acetic acid saturated with hydrogen iodide at 0° (compare Zelinsky, *Ber.*, 1902, **35**, 2678). Th

polyiodo-acetate from tetrahydrongaiol (4 g.) gave by this treatment a colourless product which still contained iodine. The reduction was completed by use of zinc dust and alcohol, yielding a product which, on hydrolysis and distillation, gave a substance which seemed to be very similar to that obtained by the direct reduction of the polyiodide with zinc dust and alcohol.

The Paraffin Alcohol, $C_{15}H_{31}\cdot OH$.—A solution of tetrahydrongaiol (12 g.) in glacial acetic acid was saturated with hydrogen iodide at −15°, and after 3 days was treated at the same temperature with zinc dust. The product was reduced as before with zinc dust and alcohol, and the resulting acetates were distilled, and treated in glacial acetic acid with hydrogen and platinum-black, 170 c.c. of hydrogen being absorbed. After filtration from the catalyst and neutralisation with sodium carbonate, the oil was extracted with ether and hydrolysed with alcoholic potash. The product was then extracted with ether and repeatedly distilled at 29 mm. pressure, giving the *alcohol*, b. p. 168—172°/29 mm., $n_D^{20°}$ 1·4474 (1·4471—1·4481), $d_{20°}^{20°}$ 0·841, whence $[R_L]_D$ = 72·64 (calc. for $C_{15}H_{31}\cdot OH$, $[R_L]_D$, 72·99) (Found: C, 78·9; H, 14·0. $C_{15}H_{31}\cdot OH$ requires C, 78·9; H, 14·1%). It did not absorb bromine from bromine water and only slowly decolorised dilute permanganate solution in the cold.

Attempt to prepare the paraffin. The impure fractions of the saturated alcohols were treated with phosphorus pentachloride, the resulting chloride was reduced with zinc dust and alcohol and with sodium and alcohol, and the product distilled repeatedly over sodium. The resulting water-white, mobile liquid (0·50 g.) had b. p. 140—145°/29 mm., $n_D^{20°}$ 1·4431, $d_{20°}^{20°}$ 0·796, and slowly decolorised permanganate (Found: C, 83·7; H, 14·0. $C_{15}H_{32}$ requires C, 84·8; H, 15·2%). The 2·3% of oxygen may be due to the presence of an ethyl ether, formed during the reduction with zinc dust and alcohol, or with sodium and alcohol (compare reduction of myrtenyl chloride; Semmler, *Ber.*, 1907, **40**, 1368). The presence of some unsaturated hydrocarbon was also evident.

Action of Hydrogen Iodide in Glacial Acetic Acid on Tetrahydrongaione.—The ketone (3·6 g.) was treated with hydrogen iodide as described above. The yellowish oil obtained soon turned red through liberation of iodine (Found: I, 55·2. $C_{15}H_{26}OI_4$ requires I, 79·6%. $C_{15}H_{26}O_2I_2$ requires I, 51·7%. $C_{15}H_{25}OI_3\cdot OAc$ requires I, 57·5%). Examination of the product of reduction (see below) showed that the substance was probably a crude tri-iodide of a keto-acetate, with which the analysis most nearly agrees. Reduction with zinc dust in the usual way gave an oil, of which the middle fraction had a saponification value of 166. The whole product was

therefore hydrolysed with alcoholic potash. Fractional distillation at 28 mm. pressure then gave three fractions, b. p. 150—170°, 170—195°, 195—, wts. 0·3 g., $n_D^{20°}$ 1·4484, 1·4529, 1·4640 (Found, respectively: C, 73·5, 76·9, 75·0; H, 11·9, 12·5, 12·2. $C_{15}H_{28}O_2$ requires C, 74·9; H, 11·7%). The first fraction was a mobile, colourless oil with an aniseed odour, the other two were yellowish, more viscous oils with fatty odours. All the fractions were unsaturated (bromine water) and yielded semicarbazones. The product of the reaction was therefore a complex mixture of keto-alcohols. The quantities of semicarbazones were too small for separation by fractional crystallisation.

Reduction of Tetrahydrongaiol with Hydriodic Acid and Red Phosphorus.—Tetrahydrongaiol (2 g.) was boiled with constant-boiling hydriodic acid (30 g.) and red phosphorus (2 g.) for 4 hours. Distillation with steam carried over a negligible quantity of light oil, which was not further examined. The heavy oily residue was extracted with ether, filtered, washed with water and alkali, dried, and freed from solvent in a vacuum over sulphuric acid (Found: I, 53·7. $C_{15}H_{30}I_2$ requires I, 54·7%. $C_{15}H_{28}OI_2$ requires I, 53·2%). Heating of tetrahydrongaiol (3 g.) under the above conditions during 20 hours with hydriodic acid gave again an oily di-iodide. It was reduced with zinc dust and alcohol in the usual way, the product was distilled in steam, extracted with ether, and divided at the ordinary pressure into two fractions, b. p. 220—240°, 240—250°, $n_D^{20°}$ 1·4465, 1·4500 (Found for the second fraction: C, 82·7; H, 13·7. $C_{15}H_{32}$ requires C, 84·8; H, 15·2%. $C_{15}H_{32}O$ requires C, 78·9; H, 14·1%). The saponification value of the acetylated product was 84. The oil was therefore a mixture of a hydrocarbon and an alcohol, the low hydrogen value indicating a cyclic or an unsaturated nature.

Colour Reactions.—Asahina, Takagi, and Hongo (*loc. cit.*, 1925; also Asano, *J. Pharm. Soc. Japan*, 1919, **454**, 99; Asahina, *Acta Phytochim.*, 1924, **2**, 1) recorded the production of a red colour when a drop of elsholtzione or atractylone was added to a solution of vanillin in concentrated hydrochloric acid. Asahina (*Acta Phytochim.*, 1924, **2**, 22) applied the reaction to a large number of furan derivatives and found that a red or red-violet colour was developed in every case with the exception of a few acids such as pyrotritaric acid.

The reaction is, however, not confined to furan derivatives, for with one exception (the oxido-glycol obtained by the hydrogenation of ngaiol with platinum-black as catalyst gave a jade-green colour) all the oxides described in this investigation have given the test. Positive tests (in some cases only after standing) have also been

given by ethyl ether, acetal, *iso*amyl ether, phenetole, anisole, diphenyl ether, and dimethylpyrone, whereas negative results were obtained with citral, citronellal, borneol, menthol, camphor, acetic anhydride, and amyl benzoate. Ordinary reagent acetone, acetaldehyde, and acetophenone gave colours indistinguishable from those given by the above oxides.

An Isomeride of Ngaiol.—The strongly odorous constituent of crude ngaiol was present also in the oil obtained after treatment with phthalic anhydride, but could be separated in the first fraction, b. p. 120—190°/29 mm., on distillation. Redistillation of this fraction led to a further elimination of the odorous constituent and the isolation of a fraction, which from its physical constants appears to be an isomeride of ngaiol, b. p. 188—190°/29 mm., $d_{20^\circ}^{20^\circ}$ 1·013, $n_D^{20^\circ}$ 1·4794 (1·4793—1·4795) (Found: C, 71·5; H, 9·6. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·5%). The substance was a light yellow liquid with a faint, sweet odour.

A Monoxide.—The proportion of crude ngaiol that would not combine with phthalic anhydride was not large, and contained generally a small amount of ngaione. From a sample (4 g.) of the lower-boiling part (b. p. 120—180°/29 mm.) a limpid, white, faintly odorous oil was obtained by distillation over sodium, at 29 mm. pressure, b. p. 160—170°, $n_D^{20^\circ}$ 1·4894 (constant over the whole fraction), $d_{20^\circ}^{20^\circ}$ 0·9485, whence $[R_L]_D$ = 67·06 (calc. for $C_{15}H_{24}O\,|\overline{1}$, 66·05; $|\overline{2}$, 67·78) (Found: C, 81·8; H, 10·8; *M*, by Rast's method, 229. $C_{15}H_{24}O$ requires C, 81·7; H, 10·9%; *M*, 220). The fraction was therefore probably a mixture of mono- and di-cyclic oxides. It took up bromine from bromine water with formation of a black oil, slowly decolorised dilute permanganate solution, developed an immediate cherry-red colour on treatment with vanillin and concentrated hydrochloric acid, and gave a violet colour in the pine-shaving test.

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CLXXVIII.—*Action of Cuprous Hydride on Diazonium Salts. A Combined Sandmeyer–Gattermann Reaction.*

By Panchanan Neogi and Anil Krishna Mitra.

The action of moist cuprous hydride (CuH) at 0° upon diazonium salts, in the presence of halogen acid and under other conditions, has been investigated. The greater part of the cuprous hydride apparently is decomposed, giving copper and cuprous halide in the reactions involving halogen acid, so that a Sandmeyer–Gattermann reaction occurs. The main organic product is the aryl halide, or a phenol from a diazonium sulphate in sulphuric acid, and diphenyl ou addition of alcohol to the sulphuric acid solution. A small quantity of the diazonium salt is, however, reduced, the corresponding hydrocarbon being formed.

Cuprous hydride, prepared by the action of an excess of hypophosphorous acid, or of sodium hypophosphite and sulphuric acid, upon a solution of copper sulphate (50—75 g.), was gradually added to the ice-cold diazo-solution. On vigorous shaking, a brisk effervescence occurred and the colour of the cuprous hydride changed slowly to an orange or reddish tint (scarlet in the case of *o*-toluidine). These colours, which were probably due to the formation of double compounds, were destroyed by washing with alcohol, ether, or acetone.

After the reaction had proceeded in the cold for 2 hours, the product was steam-distilled, washed with sodium hydroxide solution to remove phenol, dried, and fractionally distilled, or, if solid, recrystallised.

Base diazotised (g.).	Acid used.	Main product (g.).	By-product (g.).
Aniline (22)	HCl	PhCl (8·8)	PhH (1·6)
,, (15)	HBr	PhBr (9·8)	,, (1·5)
o-Toluidine (10)	HCl	*o*-C_7H_7Cl (4·5)	C_7H_8 (1·5)
o- ,, (20)	HBr	*o*-C_7H_7Br (10·6)	,, (1·8)
m- ,, (10)	HCl	*m*-C_7H_7Cl (4·2)	,, (1·3)
p- ,, (15)	HCl	*p*-C_7H_7Cl (11·3)	,, (2·1)
p- ,, (20)	HBr	*p*-C_7H_7Br (11·6)	,, (2·2)
p- ,, (15)	H_2SO_4 + KI	*p*-C_7H_7I (13·5)	,, (1·6)
Anthranilic acid (11)	HCl	*o*-$C_6H_4Cl{\cdot}CO_2H$ (7·5)	None
p-Nitroaniline (10)	HCl	*p*-$C_6H_4Cl{\cdot}NO_2$ (7·6)	,,
p-Toluidine (15)	HCl *	*p*-C_7H_7Cl (2·5)	C_7H_8 (1·7)
p- ,, (20)	HCl †	*p*-C_7H_7Cl (8·5)	None
o- ,, (15)	H_2SO_4	—	C_7H_8 (1·2)
p- ,, (15)	H_2SO_4	—	,, (2·4)
Aniline (20)	H_2SO_4 ‡	Ph·Ph (2·4)	—

* Made faintly ammoniacal; † made neutral with NaOH; ‡ alcohol added before addition of CuH.

Crystalline cuprous chloride (Found: Cu, 63·6; Cl, 35·45%) and crystalline cuprous bromide (Found: Cu, 44·1%) were obtained in the reactions between cuprous hydride and diazonium chlorides and diazonium bromides, respectively, in presence of the corresponding halogen acid. They separated after filtration of the hot solutions left in the distilling flasks, and were purified from organic substances by repeated digestion with alcohol and ether.

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CLXXIX.—*Studies of Dynamic Isomerism. Part XXVII. The Absorption Spectra of Prototropic Compounds. Physical Properties of the Stable and Labile Forms of Benzoylcamphor.*

By THOMAS MARTIN LOWRY, CHARLES ALEXANDER HAMILTON MACCONKEY, and HENRY BURGESS.

IN a paper on "Absorption Spectra and Tautomerism" (J., 1926, 706), Morton and Rosney put forward the view "that enolic and ketonic modifications possess the same wave-length of maximum absorption." As evidence in support of this conclusion they cite "the facts that addition of alkali to acetone (which presumably gives rise to a trace of an enolic salt) increases the intensity of the band, but does not produce a new band, and that the *two isomeric forms of benzoylcamphor give bands at the same wave-length, but of unequal intensity*" (p. 709). The theoretical conclusion of these authors appears to us to be very plausible, since two isomerides, which are so nearly on the same energy level that they can exist in dynamic equilibrium with each other, might very well have similar energies of activation, and therefore absorb light of similar wave-length. The observations on which they rely are, however, of a much less satisfactory character. In particular, the action of an alkali in intensifying the selective absorption of acetone is capable of alternative explanations (see especially Dawson's work on the catalysis of the iodination of acetone by acids and alkalis) and is therefore of little value as evidence in support of their conclusion; and, in the case of benzoylcamphor, the "facts" cited by the authors are in direct contradiction to measurements which had already been made by us, and which were communicated to Dr. Morton, prior to the publication of his paper. We were therefore in a position to challenge his conclusions immediately, on the basis of perfectly trustworthy data; but, in view of the obvious incompatibility of the

two sets of data, we thought it wise to postpone our criticisms until we had repeated and confirmed all our observations, and moreover had extended them in other directions to such a point that we were absolutely satisfied of their validity.

The choice of benzoylcamphor as a material for tests of this kind is justified by the exceptional stability of its two forms, which undergo isomeric change so slowly that a complete pseudobinary fusion-point diagram can be plotted for them (Vixseboxse, *Rec. trav. chim.*, 1921, **40**, 1). For the present purpose, however, where the homogeneity of the two isomerides is of crucial importance, the fact that both forms have been isolated in measurable crystals is of still greater value, since this provides an even more certain guarantee of the individuality of the preparations and of their freedom from all but isomorphous impurities. The purity of the two forms can also be checked by measurements of their initial rotatory powers in an inert solvent, as well as by the more usual method of observing their melting points when they are heated at such a rate as not to allow isomeric change to precede the melting of the compound.

The constitutions of the two forms need only be referred to incidentally, since none of the experimental data now recorded would be affected in any way if it could be shown (as Lapworth has already suggested to one of us in the case of nitrocamphor) that the two dominant forms are stereoisomeric. The structures originally assigned to them by Forster, on the basis of the ferric chloride test, have, however, been vindicated by the later work of Dimroth and of Vixseboxse, who have shown that the "enol" can be titrated sharply by Kurt Meyer's method, and that this method gives values for the equilibrium proportions of the two forms which are identical with those deduced from the optical rotations of the solutions. In the present paper, therefore, we have made use of Forster's nomenclature, and have referred to the stable and labile forms of the compound as enolic and ketonic, respectively.

The known forms of benzoylcamphor represent only two of the five theoretically possible isomerides. It is, however, unlikely that any other isomeride plays an important part in the equilibrium, since (i) the mutarotation curves are at least approximately unimolecular (see J., 1923, **123**, 2122), (ii) the percentage of enol deduced by Dimroth and Vixseboxse from bromine titrations, and by ourselves from the ratio of the initial and final solubilities of this form (p. 1344), is identical with that calculated from the optical rotatory power of the equilibrium mixture.

The measurements of absorption now described were made as part of an extensive study of the physical properties of the stable

and labile forms of benzoylcamphor, which required that we should prepare a considerable number of samples of each isomeride and satisfy ourselves at every stage that the material consisted exclusively of one or other form of the compound. Thus the earlier observations, which were communicated to Dr. Morton, were made in the course of an investigation in which we sought to establish also (i) the unimolecular character (or otherwise) of the mutarotation curves (*loc. cit.*, 1923) and (ii) the form of the curves of rotatory dispersion of the two isomerides, by extrapolation to zero time of the observed rotations for different wave-lengths. In the same way, the second series of experiments (which was undertaken primarily in order to confirm the earlier results) included the determination of *(iii) the melting points of the two isomerides under specified conditions, (iv) the initial and final rotations of the two forms, in order* to calculate the equilibrium proportions of ketone and enol in three different solvents, (v) the initial solubilities of the unchanged isomerides in these solvents, in order to test van 't Hoff's activity formula, and (vi) the initial and final solubilities of the stable enolic form, in order to determine the proportion in which it is present in the final equilibrium mixture. The numerical results of these investigations are summarised in Table I.

TABLE I.

Physical Properties of Benzoylcamphor.

		Enol.	Ketone.	Equilibrium mixture.	Equilibrium proportion of enol.
Melting point		89·5°	112°	84°	—
Specific rotation $[\alpha]_{5461}$					
in alcohol		331°	152°	258°	59%
in acetone		339°	145°	248°	53%
in benzene		315°	50°	257°	78%
Rotatory dispersion $\alpha_{4358}/\alpha_{5461}$					
in benzene at 20°		2·393	1·555	—	—
Solubility (g./100 g. solution)					
in alcohol at 17°		3·37	2·95	5·83*	58%
in acetone at 17°		19·0	19·3	36·4*	52%
in benzene at 17°		37·3	16·9	43·1*	87%
Molecular extinction coefficient in alcohol (M/10,000)				log ϵ	
1st series	λ =	3120	2475	3·95	
	log ϵ =	4·19	4·06	3·80	
2nd series	λ =	3140	2420	4·10	66%
	log ϵ =	4·27	4·21	3·90	69%

* Solid phase, the enol.

EXPERIMENTAL.

Preparation of Materials.—The work now described was delayed for many months because the published directions for making the

intermediate dibenzoyl derivative failed, in the hands of later workers, to give even the moderate yields (about 8% of the weight of camphor) which had been obtained previously. This failure was ultimately traced to the excessive care that was used to prevent the benzoylation from getting beyond control. The revised directions which have rendered the product once more available in reasonable quantities are therefore set out below, together with the methods used in preparing colourless and homogeneous samples of enolic and ketonic benzoylcamphor.

(a) *Benzoyloxybenzoylcamphene.* Flowers of camphor (150 g.) were dissolved in toluene (400 c.c.) which had been dried over sodium wire. Sodium (15 g.) was added, preferably in one piece, and heated in a flask on a water-bath under a condenser until the sodium began to melt. The flask was then removed and shaken vigorously to start the action, which was controlled by dipping the flask in ice-water. When the reaction had finished, the liquid was poured into a wide-necked bottle, which was then surrounded with ice. Benzoyl chloride (75 g.) was added in small portions, with continuous *and thorough stirring by means of a glass rod, at such a rate that* the temperature of the mixture remained between 25° and 28°. The product, which had the colour and consistency of vaseline, was allowed to stand for 2 hours, and then shaken several times with *cold water, until the latter* no longer became coloured. The toluene was recovered by distillation from a water-bath, under a pressure of about 120 mm., and the last traces of solvent were removed by reducing the pressure to 15 mm. The syrupy residue was steam-distilled until the smell of camphor could no longer be detected. If the aqueous layer deposited crystals of benzoic acid on cooling (which does not occur in a correct preparation), the syrup was freed from this acid by shaking several times with boiling water. When quite cold it was separated as far as possible from water, and just half its volume of 96% alcohol was added. After 20 hours the crystals of benzoyloxybenzoylcamphene, which in a correct preparation are already colourless, were filtered off and recrystallised from boiling alcohol.

(b) *Benzoylcamphor (enolic form).* The dibenzoyl compound (10 g.) was dissolved in alcohol (100 c.c.) and heated on a water-bath for 2 hours under reflux with a solution of sodium hydroxide (2·3 g. of sodium) in alcohol (25 c.c.) to which a little water (4 c.c.) had finally been added. The alcohol was distilled off, the last traces being removed by adding and distilling off a little water. The solid residue of sodium salts was dissolved to a cloudy solution by shaking three times with water (3 × 500 c.c.) at 80°. Colourless benzoylcamphor was then precipitated by passing carbon dioxide into the cold

filtered solution. The red tinge, which is developed when boiling water is used to dissolve the sodium salt, may be removed by dissolving the product in ether, shaking twice with water, twice with dilute hydrochloric acid (1 : 1), and again with water. The crude benzoylcamphor was crystallised from cold ether (in which solvent the equilibrium mixture contains 84% of enol) by evaporation under reduced pressure, and separated in highly refracting, colourless prisms. Further purification was effected by dissolving the compound in boiling light petroleum (or heptane) and stirring with a glass rod which had been exposed to the fumes from concentrated hydrochloric acid; the crystals, which separated slowly on cooling, were crushed and washed with ether containing a trace of hydrogen chloride.

(c) *Benzoylcamphor* (*ketonic form*). The ketonic form of benzoylcamphor was prepared by heating the enolic form (10 g.) under reflux with concentrated formic acid (20 c.c.) for 4 hours (compare Dimroth, *Annalen*, 1913, **399**, 110). After cooling (and without filtering, because there was nothing to filter), the liquid was shaken for 3 minutes with light petroleum. The precipitated crystals were drained on a Büchner funnel, washed quickly with light petroleum, shaken with water, drained, washed until all traces of formic acid had been removed, and finally dried in a vacuum over sulphuric acid. If desired, they can be recrystallised by dissolving them in ether at 20° and evaporating a part of the solvent under reduced pressure; but it was found that the melting point of the product was often lowered instead of being raised by this further treatment.

Melting Points.—Melting points of the two forms of benzoylcamphor have been given by earlier workers as follows:

	Forster.	Dimroth.	Vixseboxse.
Enol	89°	90—91°	89°
Ketone	87—88	112	107

The triple point, at which the enol crystallises from the molten equilibrium mixture, is 84°. After fusion, therefore, any chemically pure sample of benzoylcamphor will freeze at this temperature, and the melting points of both forms will tend to the same value if time is allowed for isomeric change to occur before fusion. It was therefore important to know what is the minimum time in which a melting-point tube can be heated, and its contents fused, when the temperature of the bath is higher than the melting point by a known amount. In order to obtain this information, purified acetanilide, in a fine melting-point tube, was plunged into a bath heated to different temperatures, and was found to melt in over 60 seconds with the bath at 113·9°, in about 40 seconds at 114·0°, and in about 15 seconds at 114·1° and above. These experiments

show that fusion cannot be effected in less than about 15 seconds when the melting-point tube is plunged into a bath at a slightly higher temperature, but that the lowest bath-temperature at which fusion takes place within this time is only about 0·2° above the true melting point. Under these conditions the enolic form of benzoylcamphor melts at 89·5° and the ketone at 112°. The latter temperature agrees with the melting point given by Dimroth, but, if a period of 1 minute instead of ¼ minute is allowed for fusion, the melting point is lowered by perhaps 5°, and therefore corresponds roughly with that recorded by Vixsehoxse.

The melting point given by Forster is only a little above the triple point; but this might easily be recorded as the melting point, if determined in the ordinary way, without making use of the special precautions that are needed in the case of a labile compound. For instance, when a single crystal of a sample which melted at 112° was crushed on a porous plate and heated in a melting-point tube, it melted within a minute at 90°. The substantial homogeneity of Forster's material is proved, however, by the fact that the initial rotations recorded for solutions in alcohol and in chloroform are very similar to those given in the present paper: and the complete identity of his labile material with ours is proved by the facts that the crystals belong to the same system, exhibit the same faces, and have the same axial ratios within the limits of experimental error, namely $a : b : c = 0{\cdot}7375 : 1 : 1{\cdot}0224$ (Forster) $= 0{\cdot}7454 : 1 : 1{\cdot}0138$ (L., McC., and B.).

Anthes's melting-point apparatus (*Chem.-Ztg.*, 1911, 1375), in which the liquid of the bath is made to circulate through a lateral heating-tube, was used for these experiments, but greater uniformity of temperature was secured by heating electrically instead of by a flame. For this purpose the heating-tube was wound with resistance wire and covered with Pyruma cement. The apparatus was protected from draughts by a little cardboard box with glass front and back, holes being provided in the sides of the box for the two side tubes through which melting-point tubes were immersed in the bath. When paraffin oil or concentrated sulphuric acid was used, the circulation was slow, on account of the viscous nature of the liquid; xylene (b. p. 133°), which is very mobile at 110°, was therefore used, and gave a rapid circulation and uniform heating of the thermometer. The temperature rose quickly when a heating current of about 0·5 amp. was used, and could be regulated easily to 0·1°.

Optical Rotations.—The following values have been found for the initial and final specific rotations $[\alpha]_{5461}$ of the two forms in three typical solvents ($c = 1{\cdot}25\%$ in each case).

Solvent.	Enol. Initial.	Enol. Final.	Ketone. Initial.	Ketone. Final.	Equilibrium mixture, %. Enol.	Equilibrium mixture, %. Ketone.
Alcohol	331°	258°	152°	258°	59	41
Acetone	339	248	146	249	53	47
Benzene	315	256	50	257	78	22

It will be seen that the rotatory power of the enolic form is very similar in all three solvents, but that the ketone has a much lower rotatory power in benzene than in acetone or alcohol. A similar contrast is seen in the proportions of enol and ketone in the equilibrium mixture, which show clearly that the two oxygenated solvents favour the formation of the ketone in a much higher degree than does the hydrocarbon. The correlation of this displacement of equilibrium with the relative solubilities of the ketone and enol in the three solvents is discussed below.

Rotatory Dispersion.—The rotatory dispersions of the enolic and ketonic forms of benzoylcamphor were measured in 6-dcm. tubes at 20° in pure benzene. The concentrations of the solutions were as follows :

Enolic benzoylcamphor, 8·000 g. in 52·242 g. of solution :

$d_{4^\circ}^{20^\circ} = 0{\cdot}9075$, hence $c = 13{\cdot}90$ g./100 c.c. : $[\alpha] = 1{\cdot}199\ \alpha$.

Ketonic benzoylcamphor, 8·000 g. in 61·7075 g. of solution :

$d_{4^\circ}^{20^\circ} = 0{\cdot}9034$, hence $c = 11{\cdot}71$ g./100 c.c. : $[\alpha] = 1{\cdot}423\ \alpha$.

Since each form changed into the other during the determinations, the observed rotations had to be corrected in order to give the rotatory power of the pure compounds. For this purpose the rotation of each form for the line Hg 5461 was measured at intervals during the experiment and plotted against the time. The amount of ketone and of enol present at the time of each determination could be read off from the graph and the rotation of each form at zero time could then be calculated. In the case of the enol, the correction, even of the latest readings, is probably accurate within $\pm$ 0·5°; that of the earliest readings, *e.g.*, those taken with the mercury lines, is proportionally more exact. In the case of the ketone, the error from this source should not be larger than 0·1° for the three mercury lines, which were read first, and about 0·25° for two copper yellow lines and the zinc red line, which were read next, but the solution had then changed so much that no further readings were taken; the values used to correct the rotations of the enolic form were therefore interpolated from a curve of rotatory dispersions, on which the rotations of the mercury lines and the zinc red line were plotted. The observed and corrected rotations are set out in Table II,

together with values for the specific rotation of the enolic forr calculated from the formula

$$[\alpha] = \frac{80 \cdot 82}{\lambda^2 - 0 \cdot 10023} - \frac{27 \cdot 65}{\lambda^2}.$$

The rotatory dispersion of enolic benzoylcamphor can be express(quite satisfactorily by means of a three-constant formula, sinc even on specific rotations of several hundred degrees, the diffe ence between the (corrected) observed and calculated values is alwa; less than a degree. Since the second dispersion constant is ignor(in a three-constant equation, the value of the first dispersion consta: is not very trustworthy; but the characteristic wave-lengt $\lambda = 3160$, deduced from the equation agrees closely with t observed head of the absorption band at 3100 or 3140 Å.U. It moreover, noteworthy that the difference is similar in direction t although substantially smaller in magnitude than, that which h already been recorded in camphorquinone and in camphor, where amounts to about 70 Å.U. (J., 1924, **125**, 2521; 1925, **127**, 61] as well as in the halogen derivatives of camphor, which produce much stronger "general absorption" than camphor and give discrepancy of about 140 Å.U. The same explanation of the discre ancy may therefore be adopted, namely, that "when a selecti absorption is superposed on a strong general absorption, the observ head of the band will be displaced to a region of shorter wav lengths" (J., 1925, **127**, 1267).

The rotatory dispersion of the ketone is in striking contra with that of the isomeric enol. Thus the rotation of the en increases rapidly as the wave-length decreases, and tends towar an infinite positive value at the absorption band; moreover, sin the rotation constant of the positive low-frequency term is thr times as great as that of the negative high-frequency term, t! rotation must remain positive over the whole range of wave-lengtl the rotatory dispersion being therefore "complex but normal In accordance with this behaviour the dispersion ratio $[\alpha]_{435}$ $[\alpha]_{5461}$ of the enol is as high as 2·393; that of the ketone, on the oth hand, is only 1·555. The latter value agrees closely with the the retical ratio 1·57 for a substance obeying Biot's law of inver squares, $\alpha = k/\lambda^2$, where k has the value 18·04. In this respe(therefore, the rotatory dispersion of the ketone is similar to th of sodium tartrate (Lowry and Austin, *Phil. Mag.*, 1922, *A*, **22** 249) and of octyl oxalate (Lowry and Richards, J., 1924, **12** 1596). Since, however, this value for the dispersion ratio could on be reached if the nearest absorption hand were at zero wave-leng (and smaller values would make the characteristic wave-length

imaginary quantity), it is evident that the apparent simplicity of the dispersion law is only an approximation resulting from a balancing of two partial rotations of opposite sign. In the two cases cited above, this complexity was made obvious by small, systematic deviations from the calculated rotations; in the present instance there are not enough data to show these small deviations, but, since the dispersion ratio is actually less than the theoretical minimum, it is clear that the rotations can only be expressed by a two-term equation, with terms of opposite sign. It can, indeed, be predicted with some confidence that the rotatory dispersion would become anomalous in the ultra-violet region, and undergo a reversal of sign as the ketonic absorption band at $\lambda = 2480$ Å.U. is approached, since this predicted anomaly has already been verified experimentally in the case of sodium tartrate.

TABLE II.

Rotatory Dispersion of Benzoylcamphor in Benzene at 20°.

	(a) Ketonic form.				(b) Enolic form.					
Wave-length.	t (min.).	$[\alpha]$ (obs.).	Correction.	$[\alpha]$ (corr.).	t (min.).	$[\alpha]$ (obs.).	Correction.	$[\alpha]$ (corr.).	$[\alpha]$ (calc.).	Diff.
Cd 6438	—	—	—	+*42·2* *	241	+188·72	+1·90	+190·6	+190·4	+0·2
Zn 6362	116	+45·97	−2·17	+42·8 }	53	196·79	0·25	197·0	197·1	−0·1
	91	+44·84	−1·54	+43·3 }						
Na 5893	—	—	—	+*51·3*	—	—	—	*255·6*	—	—
Cu 5782	105	+57·31	−3·21	+54·1	111	261·58	0·90	262·5	262·5	±
Hg 5791	75	+54·29	−0·99	+53·3 }	28	262·65	0·16	262·8	262·8	±
Hg 5770	54	+53·65	−0·25	+53·4 }						
Cu 5700	110	+58·85	−3·95	+54·9	117	274·17	1·00	275·2	274·6	+0·6
Ag 5465	—	—	—	+*60·2*	228	311·78	2·95	314·7	314·6	+0·1
Hg 5461	49	+60·77	−0·27	+60·5	46	315·22	0·29	315·5	315·5	±
Cu 5218	—	—	—	+*67·2*	73	367·44	0·75	368·2	368·2	±
Cu 5153	—	—	—	+*69·2*	84	384·11	0·95	385·0	384·7	+0·3
Cu 5106	—	—	—	+*70·6*	95	395·61	1·15	396·8	397·7	−0·9
Cd 5086	—	—	—	+*71·4*	258	398·48	4·69	403·2	403·2	±
Zn 4811	—	—	—	+*81·0*	68	495·47	0·94	496·4	496·6	−0·2
Zn 4722	—	—	—	+*84·3*	123	532·26	2·20	534·5	534·4	+0·1
Hg 4358	62	+95·52	−1·42	+94·1	37	753·77	0·72	754·5	755·2	−0·7
Hg 5461	66	+61·19	—	—	24	315·16	—	—	—	—
,,	82	+62·29	—	—	139	314·05	—	—	—	—
,,	163	+71·98	—	—	148	313·81	—	—	—	—
,,	174	+73·84	—	—	188	313·31	—	—	—	—
,,	—	—	—	—	198	313·10	—	—	—	—
,,	—	—	—	—	308	310·26	—	—	—	—
,,	—	—	—	—	321	310·17	—	—	—	—

* Extrapolated or interpolated values are shown in italics.

Solubilities.—When dissolved in an inert solvent of reasonable purity, and at a low temperature, the two forms of benzoylcamphor are converted into each other so slowly that it is possible to measure, not only the solubility of the stable form before and after isomeric change has taken place (as described in Parts II and III of this series, J., 1904, **85**, 1541, 1551), but also the initial solubility of the labile ketonic form. Benzoylcamphor was therefore selected by Dimroth (*Annalen*, 1913, **399**, 110) as a suitable substance with which to test the theorem of van 't Hoff, that the change of equilibrium due to the solvent is completely allowed for when " the unit

of concentration is no longer the gram-molecule per litre, but the concentration of the saturated solution " ("Vorlesungen," 1898, I, 217; English trans., p. 221), or, as Dimroth expresses it, " two interchangeable isomers, desmotropes or tautomers are in equilibrium in any solvent, when their concentrations are in the same proportions to one another as their solubilities in that solvent, multiplied by a constant *G*." Thus $c_A/l_A = G \times c_B/l_B$, or $c_A/c_B = G \times l_A/l_B$, where c_A and c_B are the concentrations, and l_A and l_B the solubilities of the two forms in a given solvent, and *G* is a function of the vapour pressures of the two forms and of their equilibrium concentrations in the vapour, but is independent of the solvent.

Van 't Hoff's theorem (which does not allow of a reversal of solubility by change of solvent) is obviously not applicable in the case of *iso*nitrosomalonanilide, which crystallises from alcohol, ether, ethyl acetate, or acetic acid in white, pearly scales, but from chloroform or benzene in yellow needles (Whiteley, J., 1903, **83**, 34), nor in the case of nitroformaldehydehydrazone, which separates in the α-form from benzene, chloroform, or light petroleum, but in the β-form from water or alcohol (Bamberger, *Ber.*, 1901, **34**, 2001). Dimroth, however, found the following ratios for the two forms of benzoylcamphor at 0°, and concluded that " van 't Hoff's theorem *is completely confirmed*."

	c_A/c_B.	l_A/l_B.	*G*.
Ether	6·81	6·39	1·06
Ethyl acetate	1·98	1·81	1·09
Ethyl alcohol	1·67	1·57	1·06
Methyl alcohol	0·87	0·748	1·15
Acetone	0·853	0·80	1·06

Vixseboxse, on the other hand, after measuring the concentration ratios and the solubility ratios in three solvents at 17°, found that the value of *G* varied from 1·13 to 1·52, and concluded that " *G* is therefore not constant " (Dissertation, Amsterdam, 1919; compare *Rec. trav. chim.*, 1921, **40**, 1).

Since these two authors arrived at opposite conclusions from the study of the same compound, we thought it desirable to make use of the experience which we had gained in the isolation of the two pure isomerides in order to carry out measurements of solubility under similar conditions to those used by Vixseboxse. For this purpose the purified material was crushed in an agate mortar and stirred vigorously with 5 c.c. of solvent in a vessel mounted in a thermostat; a sufficient quantity of solid was used to make the liquid cloudy, but a little fine powder was added 2 minutes before a sample of the saturated solution was taken for analysis, in order to ensure saturation. The sample was removed by means of a 1 c.c. pipette, with a piece of filter paper wired over the tip; it was

transferred to two weighing bottles, evaporated in a current of air, and finally dried for 18 hours over sulphuric acid and paraffin wax in a vacuum desiccator. The time at which samples were taken was fixed at 8 minutes, after a trial run with enolic benzoylcamphor in ethyl alcohol at 15°, which gave the following solubilities :

Time (mins.)	4½	9	13½	30
Conc. (g./100 g. of solution)	3·1	3·1	3·0	3·7

The solubilities found in this way are set out in Table III, where the subscripts A and B relate to enol and ketone, respectively, and the figures shown in parentheses are data cited from Vixseboxse's paper or read off from his graphs.

TABLE III.

Solubility of Benzoylcamphor at 17°.

	Solubility, g. per 100 g. of solution.			Solubility, mols. per 100 mols. of solution.				
Solvent.	Enol.	Ketone.	Ratio.	l_A.	l_B.	l_A/l_B.	c_A/c_B.	*G*.
Alcohol	3·37	2·95	1·14	0·62	0·54	1·15	1·44	1·25
				(0·71)	(0·58)	(1·22)	(1·56)	(1·28)
Acetone	19·0	19·3	0·98	5·05	5·1	0·99	1·12	1·13
				(5·0)	(5·2)	(0·96)	(1·08)	(1·13)
Benzene	37·3	16·9	2·21	15·3	5·8	2·64	3·55	1·34
Toluene	—	—	—	(12·1)	(4·1)	(2·95)	(4·56)	(1·52)

In the case of acetone our ratios agree throughout with those of Vixseboxse, and give an identical value for the constant $G = 1{\cdot}13(1{\cdot}13)$. In the case of alcohol, our solubilities are slightly lower, but lead to almost the same value for $G = 1{\cdot}25(1{\cdot}28)$. The solubilities in benzene and toluene do not afford any similar check on one another; but they concur in giving a higher value for the constant $G = 1{\cdot}33$*$(1{\cdot}52)$. The concordance of the values given by Vixseboxse and by ourselves for solutions in acetone and in alcohol shows that the difference in the magnitude of the constant in these two solvents is real; it is also clear that the aromatic hydrocarbons give still higher values. Van 't Hoff's theorem is therefore not an exact relationship; but, since the three values which we have obtained cover a range of only ± 8%, we can at least regard it as a good first approximation.

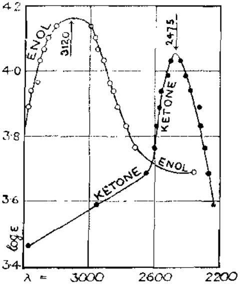
As a further check on the composition of the equilibrium mixture, we have determined the ratio of the initial and final solubilities of the enol in alcohol, acetone, and benzene. The results are included in Table I, but alcohol is the only solvent in which the solubility is sufficiently low to permit of a trustworthy deduction of the equilibrium ratio from the solubilities. The ratio of the initial to

* This value would be increased to 1·6 if the solubilities were expressed in g. per 100 g. of solution instead of in mols. per 100 mols.

the final solubility (*viz.*, 3·37/5·83) in this solvent indicates that there is 58% of enol in the equilibrium mixture; this proportion agrees closely with the value, 59%, deduced from the optical rotations, and therefore indicates (but does not prove) that only the two known isomerides play any important part in the final equilibrium.

Absorption Spectra.—The first series of absorption spectra were measured with a sector-photometer and a quartz spectrograph (compare Lowry and French, *Proc. Roy. Soc.*, 1924, *A*, **106**, 489), *N*/10,000 alcoholic solutions being used. The absorption curves (Fig. 1) show a very strong enolic band, the molecular extinction coefficient rising to a maximum log ε = 4·19 at 3120 Å.U. The pure ketone, on the other hand, gave a band of its own with a maximum log ε=4·06 at 2475 Å.U. The optical purity of the two specimens is shown by the fact that the molecular extinction coefficient of the enol passes through a *minimum* at a wave-length near to that at which the absorptive power of the ketone rises to a *maximum*, and conversely that the absorptive power of the ketone falls rapidly throughout the region in which that of the enol is rising from a minimum at 2570 to a maximum at 3100 Å.U. The equilibrium mixture of the two forms showed both maxima, the enolic band giving a maximum log ε = 3·95 at 3100 Å.U. and the ketonic band a maximum log ε = 3·80 at 2475 Å.U.

FIG. 1.
Extinction coefficients of benzoyl-camphor.
(*First series: sector-photometer.*)



These observations showed clearly that, in direct opposition to Morton and Rosney's statement, the intensities of the absorption bands of the two forms were approximately equal to one another, whilst the frequencies were quite different; but in order that there should be no possible doubt as to which series of data is correct, the whole of the work was repeated with fresh materials, as part of a more extensive investigation of the physical properties of the two isomerides. In this case an ultra-violet spectro-photometer was used in place of the sector-photometer, since the data given by the latter may be influenced by the characteristic curve of the photographic plate. The results of this second series of measurements are plotted in Fig. 2. The enol now shows a maximum, log ε

= 4·27 at 3140 Å.U., whilst the ketone gives a maximum at log ε = 4·21 at 2420; in the equilibrium mixture, the enolic band gave a maximum at log ε = 4·10 and the ketonic band at log ε = 3·90. No trace of the enolic band was detected in solutions of the pure ketone when the observations were completed in a sufficiently short period of time to avoid the occurrence of isomeric change; but the enolic band was readily observed in specimens which had partly

FIG. 2.

Extinction coefficients of benzoyl-camphor.

(*Second series: spectro-photometer.*)

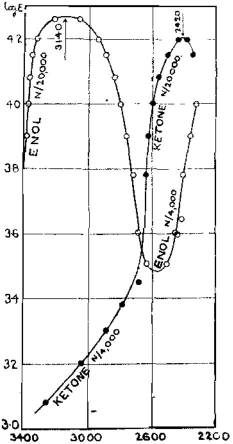
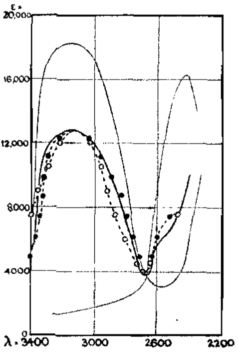


FIG. 3.

Extinction coefficients of equilibrium mixture.

(*Full line = calculated values; broken lines = observed values.*)



reverted to the enolic form on storage, and it was always seen in solutions which had been kept long enough to allow of a partial isomeric change.* The fact that Morton's specimen of the ketone

* The enolic band, in a mutarotating solution of the ketone, was first recorded after ½ hour at λ = 2860, log ε = 3·36, and then drifted across slowly to the normal wave-length λ = 3140 and intensity log ε = 4·1 of the band in the equilibrium mixture. It was also noticed that the extinction coefficient for the wave-length λ = 2660 (at which the values for the ketone, enol, and equilibrium mixture are identical at log ε = 3·6) appeared to pass through a minimum value, instead of remaining constant, during the mutarotation of the enolic form.

gave a weak band at the wave-length of the enolic maximum could be explained by supposing that his solution contained some of the more stable enolic isomeride; but it is more surprising that he makes no mention of the band at 2420 Å.U., since this is only slightly less intense than the enolic band itself.*

Although the visual readings of a spectrophotometer plate are not of a high order of accuracy, the fact that they give numerical values for the molecular extinction coefficient of the solute makes it possible to use them as the basis of an independent determination of the proportions of enol and ketone in the equilibrium mixture. Thus, if we select for examination the extinction coefficients at wave-lengths corresponding with the enolic and ketonic maxima respectively, we obtain the following results :

	Molecular extinction coefficients.			Equilibrium ratio.	
Wave-length.	Enol.	Ketone.	Equilibrium mixture.	Enol.	Ketone.
$\lambda = 3140$	18,400	1,300	12,600	66	34
$\lambda = 2420$	4,300	16,200	8,000	69	31

The equilibrium ratio deduced by Dimroth and by Vixseboxse from bromine titrations was 61 : 39 for saturated solutions in alcohol, and this agrees closely with the ratios 60 : 40 and 59 : 41 deduced by Vixseboxse and by ourselves from observations of optical rotatory power. The ratios deduced from the absorption spectra for alcoholic solutions of about $M/20{,}000$ concentration show a higher percentage of enol, but, since they agree very well with one another, this higher ratio may be regarded as a definite change of equilibrium resulting from the extreme dilution of the solution.

Summary.

(*a*) Measurements have been made of the melting point, optical rotation, rotatory dispersion, solubility, and ultra-violet absorption of the stable and labile forms of benzoylcamphor.

(*b*) Contrary to an earlier statement "that the two isomeric forms of benzoylcamphor give bands at the same wave-length, but of unequal intensity," it has been found that the absorption bands are of nearly the same intensity, but differ widely in wave-length. The absorption of the equilibrium mixture in very dilute alcoholic solutions corresponds closely with that of a mixture of two parts of enol and one part of ketone.

* [Note added, *May 11th*, 1928.] Dr. Morton has been kind enough to prepare fresh samples of the two isomerides from a specimen of crude benzoylcamphor which we sent to him, and has confirmed the general form of the absorption spectra recorded in Fig. 2. The origin of the different results recorded previously is under investigation.

(c) Van 't Hoff's relation between the solubilities of the two forms and their equilibrium concentrations has been tested for solutions in alcohol, acetone, and benzene, and found to hold good within ± 8%.

(d) The ratio of the initial and final solubilities of the enolic form indicates that the equilibrium mixture in a saturated alcoholic solution contains about 58% of enol, in close agreement with the proportion, 59%, deduced from the optical rotations of the solutions.

We are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of us (C. A. H. McC.) with the help of which the experimental work described in the present paper was carried to completion.

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CLXXX.—*Optical Activity and the Polarity of Substituent Groups. Part VIII. Growing-chain Effects and the* ortho-*Effect in Benzoic Esters.*

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IN earlier communications of this series (J., 1926, 553; this vol., p. 178) it has been established that a group which is *m*-directive in benzene substitution raises the rotatory power of menthyl or *sec.*-β-octyl benzoate when introduced into the ortho-position to the carboxylic complex, and that an *o,p*-directive substituent in this position lowers the rotation. The magnitude of the resulting change has also been shown to be related directly to the magnitude of the directive power of the group on benzene substitution.

An effect of this kind must be transmitted to the asymmetric centre either through the chain of intervening atoms or directly through space. The former supposition is favoured by the similarity in the influence of the substituents on rotatory power and on benzene substitution, since orientation effects in benzene substitution are commonly explained by electronic rearrangements which are assumed to be transmitted through the nucleus (Robinson, *J. Soc. Chem. Ind.*, 1925, **44**, 456; J., 1926, 401; Ingold and Ingold, *ibid.*, p. 1310. Compare also Højendahl, J., 1924, 1381, on alternation in an aliphatic chain). On the other hand, the fact that substituents in the *m*- and *p*-positions do not produce the same type of change in rotatory power (this vol., p. 178) is strongly against this view. There remains the possibility that the influence in question is propagated

directly through space. In this case a similar effect on the rotatory power should be evident in other compounds the stereochemical configuration of which is such as to bring the substituent into close proximity to the asymmetric group. Numbered among such compounds are the *o*- and *peri*-derivatives of naphthoic esters (to be dealt with in a subsequent communication) and the homologous series of esters of aliphatic acids containing the substituent as a terminal group in the alkyl radical. In the latter compounds the terminal group returns on itself at regular intervals as the chain increases in length, often giving rise to characteristic maxima or minima at intervals of about 5 carbon atoms. If, therefore, the *o*-effect in the benzoic esters is transmitted through space, it would be anticipated that similar differences would be exhibited in the behaviour of growing chains possessing terminal groups of different types.

An attempt has now been made to obtain further evidence bearing on this point by the investigation of two series of optically active esters, the menthyl *n*-alkyloxyacetates and the menthyl hydrogen esters of *n*-dicarboxylic acids. Of these, the former has a terminal group which is *o*-*p*-directive in type, and the latter has one which is *m*-directive. The values obtained for the rotatory powers of these esters in the homogeneous state and in solution are summarised in Tables I and II. Values observed for other temperatures and wave-lengths are given in the experimental section. All the following rotations are negative in sign.

I. l-*Menthyl* n-*Alkyloxyacetates*, $C_{10}H_{19}O{\cdot}CO{\cdot}CH_2{\cdot}OR$.

R.	Me.*	Et.*	Pr.	C_4H_9.	C_5H_{11}.	C_6H_{13}.	C_7H_{15}.	C_8H_{17}.
$[M]_{5461}^{20^\circ}$	195·3°	189·6°	187·4°	189·2°	189·0°	186·8°	186·1°	186·2°
$[M]_{5461}^{90^\circ}$	193·6°	193·1°	191·3°	192·3°	191·0°	188·6°	188·1°	188·7°
$\frac{\alpha_{4358}}{\alpha_{5893}}$ (20°) ...	1·968	1·962	1·967	1·964	1·963	1·964	1·964	1·963

* Rule and Smith, J., 1925, **127**, 2188.

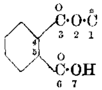
II. *Values of* $[M]_{5461}$ *for the* l-*Menthyl Hydrogen Dicarboxylates in the Homogeneous State and in Solution* (*approx.* 5%).

						Sodium salt in	
n.	Homog., 20°.	Homog., 60°.	In C_6H_6.	In EtOH.	In $CHCl_3$.	water.	alcohol.
6	189·9°	188·3°	183·8°	195·1°	203·3°	195·4°	—
7	—	—	180·4*	—	199·7*	193·6	—
8	191·9	191·1	198·4	200·2	203·2	189·5	198·3°
9	185·6	184·9	193·1	195·4	199·0	186·4	197·1
10	186·6	185·3	192·1	198·8	198·3	183·5	197·1
11	183·0	181·7	188·5	194·1	196·3	176·4	198·2
12	192·6	—	197·6	200·1	—	181·0	198·9
13	187·8	—	195·3	199·4	—	179·7	196·9

* Kenyon and Pickard, J., 1915, **107**, 54.

Except in a few instances the rotatory powers were measured over the range λ_{4358} to λ_{6708}, and in every case the values of $1/\alpha$ plotted against λ^2 gave a straight line. The esters therefore exhibit normal and simple dispersion under the conditions of experiment. The dispersion ratios $\alpha_{4358}/\alpha_{5893}$ for both series of compounds approximate closely to 1·96. As may be seen from the tables, a change of temperature has little effect on the rotatory power. The values for the alkyloxy-esters rise slightly with increase in temperature, whereas those for the dicarboxylates fall somewhat.

Comparison of the Rotation Curves.—The influence of the growing chains on the rotatory powers of the esters is illustrated in Fig. 1, in which the length of the chain, n, is measured from and including the asymmetric atom (terminal hydrogen being omitted). As will be seen from the following formulæ, the growing chain of each series resembles that of menthyl hydrogen phthalate in containing two oxygen atoms.

Menthyl hydrogen glutarate.	Menthyl propoxyacetate.	
C–O–C(O)–CH_2–CH_2–CH_2–C(O)–OH 1 2 3 4 5 6 7 8	C–O–C(O)–CH_2–O–CH_2–CH_2–CH_3 1 2 3 4 5 6 7 8	

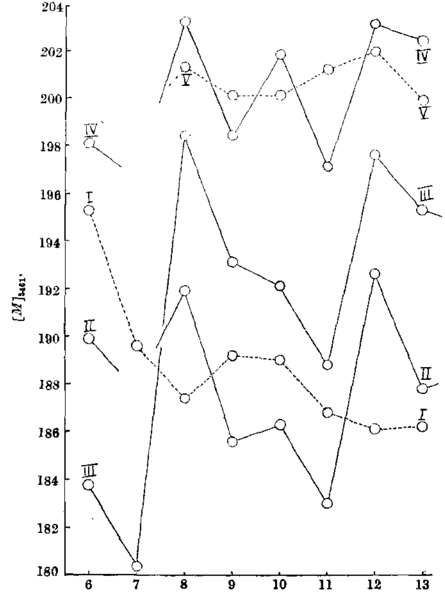
A striking difference between the two curves, which leaps at once to the eye, is the regular and pronounced alternation of the carboxy-compounds. Apart from this, however, the visible portions of the two sets of diagrams stand in the strongest possible contrast with one another. The values for the alkyloxyacetic esters fall steeply to a minimum at $n = 8$, rise rapidly to a maximum at $n = 9,10$, and then fall again to a minimum at $n = 12,13$. The values for the menthyl hydrogen carboxylates, on the contrary, rise to a maximum at $n = 8$, descend to minimum values at $n = (9),10,11$, and finally rise towards a maximum in the neighbourhood of $n = 12$. Except for a slight lack of exact correspondence in the central portion of the diagrams, due to the strongly alternating character of one of them, the maxima for the one series coincide with minima for the other, and *vice versa.*

Reference to the numbering diagram given above for the *o*-benzoic ester shows that the high value of the phthalate and the low value of the *o*-methoxy-ester occur at chain length $n = 7$, whereas the corresponding maximum and minimum points in Fig. 1 occur at $n = 8$. The discrepancy may possibly be explained by the fact that the interior angle between the valency bonds of the benzene ring is greater than that existing in a strainless compound; this brings the *o*-groups closer together than would be the case with the normal bending of an aliphatic chain and thus tends to

accelerate the occurrence of the characteristic maximum or minimum values.

As might be expected, the magnitude of the *o*-effect in the benzoic

FIG. 1.



I *Menthyl alkyloxyacetates* (*homog.* 20°). II *Menthyl hydrogen dicarboxylates* (*homog.* 20°). III *Menthyl hydrogen dicarboxylates* (*in* C_6H_6). IV *Dicarboxylates* (*in* EtOH). V *Dicarboxylates* (*sodium salt in* EtOH).

For rotations in alcohol subtract 3° *from scale value.*

esters is large compared with the deviations in the curves for the aliphatic esters. In the benzene derivatives the configuration of the molecule is such that the substituent group is permanently maintained at the most effective distance from the asymmetric atom.

In the aliphatic compounds the chain is probably in a state of constant motion, and the particular formation in which the end of the chain is so twisted as to be in spatial proximity to the asymmetric atom is only one of many arrangements assumed by the molecule. In this case, therefore, the spatial influence of the terminal group is very much weaker. Another factor which tends further to diminish the spatial influence in the alkyloxy-series is that the polarity of the terminal substituent becomes weaker as the chain lengthens. Indeed, in the longer chain compounds of this type under examination, the spatial effect of the terminal group is in all probability scarcely influenced by the presence of the oxygen atom.*

The above interpretation of the variations in the rotatory powers of the alkyloxyacetic esters is based on the assumption that these are caused by the end of the chain returning to the neighbourhood of the asymmetric atom or the adjacent oxygen atoms. But the possibility cannot be excluded that some of the observed changes are secondary effects due to the chain returning on the oxygen atom of the alkyloxyl group. The maximum at $n = 9,10$, for example, in so far as the length of the chain is considered, might equally well be due to either of these causes. The probabilities, however, point to the original assumption being correct. If the effect were a secondary one it would be expected to be small, since such an influence must necessarily be weakened by subsequent transmission through the chain from the O-atom to the asymmetric centre. On the contrary, the maximum shown in the diagram, although much less than the corresponding changes in the dicarboxylic esters, is scarcely smaller than would have been anticipated considering that we are comparing the influence of a comparatively inactive alkyl group with that of the highly active oxygen of the carboxyl group.

Further evidence on this point may be drawn from the dissociation constants of acids of the type of crotonic acid. As is well known, the commoner substituents with the exception of alkyl and amino-groups lead to an increase in acidic strength when introduced into an organic acid. Superimposed on this *general effect*, however, a secondary effect may sometimes be observed. This appears to be similar to that present in the above optically active compounds, in which the carboxyl group produces a change in the opposite sense

* The menthyl esters of *n*-aliphatic acids unfortunately give a rotation-curve in which the changes produced by the growing chain are small and irregular. A series of esters of ω-methoxy-aliphatic acids would have offered the ideal contrast with the above menthyl hydrogen dicarboxylates, but as their preparation presented too many difficulties the alkyloxyacetic esters were selected in the expectation of obtaining a series with well-defined maxima and minima.

to that given by CH_3, OH, or Cl, and is illustrated by the following dissociation constants taken from Landolt–Börnstein's "Tabellen." In these geometrical isomerides, and also in the phenyloximinoacetic acids, the spatial proximity of a CH_3, OH, or Cl to the carboxyl group lowers the acidic strength. In maleic and fumaric acids, and similar compounds, the juxtaposition of a second carboxyl group raises the acid strength.

H·C·CH₃	CH₃·C·H	CH₃·C·Cl	Cl·C·CH₃
‖	‖	‖	‖
$H·C·CO_2H$	$H·C·CO_2H$	$H·C·CO_2H$	$H·C·CO_2H$
Crotonic acid, $0·22 \times 10^{-4}$.	*iso*Crotonic acid, $0·36 \times 10^{-4}$.	β-Chloro*iso*crotonic acid, $0·95 \times 10^{-4}$.	β-Chlorocrotonic acid, $1·44 \times 10^{-4}$.

$C_6H_5·C·CO_2H$	$C_6H_5·C·CO_2H$	$H·C·CO_2H$	$H·C·CO_2H$
‖	‖	‖	‖
N·OH	HO·N	$HO_2C·C·H$	$H·C·CO_2H$
Phenyloximinoacetic acids, 18×10^{-4}.	155×10^{-4}.	Fumaric and maleic acids, 10×10^{-4}.	150×10^{-4}.

On the whole, the available evidence supports the view expressed above that *the opposite character of the two sets of diagrams in Fig. 1 is due to the dissimilar spatial influences exerted on the asymmetric atoms by the terminal groups of the growing chains.*

The irregular nature of these influences suggests one reason for the failure which has attended so many attempts to establish constitutional regularities in the domain of optical activity, and also explains some of the minor discrepancies observed in cases where such regularities have been successfully traced. In the sequence of groups representing the *general polar effect* of substituents on the rotatory powers of the menthyl esters, $XCH_2·CO·O·C_{10}H_{19}$, *viz.*, CN>Cl>Br>OH>OMe>Me>CO_2H>H, the carboxyl was found to take an unexpectedly low place (Rule and Smith, J., 1925, **127**, 2188). This is now readily understood on reference to the diagram, in which menthyl hydrogen malonate, $n = 6$, is seen to occupy a minimum with the methoxyacetate, $n = 6$, on a corresponding maximum.

Alternation in the Menthyl Hydrogen Dicarboxylates.—The menthyl hydrogen dicarboxylates exhibit marked alternation in rotatory powers, both in the homogeneous state and when dissolved in benzene or chloroform. In alcoholic solution, in which the maxima at $n = 8$ and 12 are much less marked, the alternation becomes exceptionally prominent. This behaviour is in strong contrast with that of the dimenthyl esters, which show no alternation (Hall, J., 1923, **123**, 109). Similarly, no alternation has been observed for the corresponding dioctyl esters in the homogeneous state or in alcoholic solution, although it becomes feebly evident in carbon disulphide solution (Hall, *ibid.*, p. 32). In each of the above cases

where alternation is present, the compounds derived from acids having an odd number of carbon atoms possess a higher rotation than those derived from even acids.

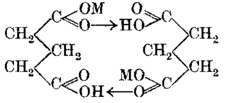
The rhythmic deviations in the rotation curve of a homologous series have been explained as space effects due to the spiral twisting of the growing chain. A regular alternation from member to member, on the other hand, may be caused by the zig-zag conformation of the chain leading to an alternate *cis*- and *trans*-structure of the molecule. Odd members of the above ester series, on this assumption, would have the terminal carboxyls in the *cis*-position to one another. As has already been seen in the cases of menthyl hydrogen glutarate and azelate, and of the analogous menthyl and *sec.*-β-octyl hydrogen phthalates, this spatial proximity would lead to an enhanced rotatory power and thus be in agreement with the experimental facts. Although it seems quite possible that structural changes of this kind may serve to explain the minor alternations visible under special conditions in the above-mentioned dioctyl esters, the magnitude of the alternation in the menthyl hydrogen carboxylates is greater than would be anticipated on this score. Moreover, these considerations do not appear to offer any reason for the complete disappearance of alternation when the ester-acids are examined in the form of their sodium salts. In aqueous solution, the values for the salts fall steadily, giving practically a straight line except for a minimum at the suberate ($n = 11$). At first it was thought that this unexpected result might be connected with the use of water as solvent, and as many as possible of the rotatory powers were therefore repeated with alcohol as solvent, in which both the ester-acids and their salts are soluble. It was then found that the salts gave a smooth curve following the mean trend of the strongly alternating values of the free acids (see Fig. 1) with corresponding, although not very marked, maxima at the glutarate ($n = 8$) and azelate ($n = 12$). In menthyl phthalate the presence of the free $\cdot CO_2H$ group raises the rotatory power, whereas that of the ionised $\cdot CO \cdot O'$ group lowers the activity. These groups also produce opposite types of orientation effects in benzene substitution. Hence it was expected that the salts of the menthyl hydrogen dicarboxylates would yield a curve with minima at $n = 8$ and 12, in contrast with the maxima given by the parent acids. Although the general form of the curve in the non-dissociating solvent benzene (III) becomes progressively flatter as it passes through chloroform to the homogeneous state (II) and the strongly ionising solvent alcohol (IV), the maxima still remain evident, even when the compounds are examined in the form of their salts (V).

The disappearance of alternation in the ionised compounds,

coupled with the persistence of the maxima, is not readily explained by the simple *cis*- and *trans*-variation in structure outlined above. These facts suggest that the diagrams for the dicarboxylic esters represent the summation of two main disturbances, and that superimposed on the influence of the returning chain is a second effect caused by molecular association through the medium of the carboxyl groups. It is known from the *X*-ray analysis of the solid higher fatty acids that they are associated into double crystal cells (Müller and Shearer, J., 1923, **123**, 3156), and in order to explain the alternation in the molecular heats of these compounds Garner and Randall (J., 1924, **125**, 881) conclude that this association may take place in two ways, according as the acids contain an even $\left(R{\cdot}C{<}^{OH\ \ O}_{O\ \ HO}{>}C{\cdot}R\right)$ or an odd number $\left(R{\cdot}\underset{O}{\underset{\|}{C}}{-}OH\ \ O{=}\overset{HO}{\overset{|}{C}}{\cdot}R\right)$ of carbon atoms. Now if reference be made to the figures recorded by these authors it will be seen that the odd acids, which have the higher specific heats in the solid state, have also the higher values in the liquid condition, although the alternation from odd to even in the liquids is much less pronounced. If, therefore, the alternation in the solid state is due to the two different forms of association suggested, the same difference of structure must exist to a lesser extent in the liquid phase. In this case it is possible to explain not only the alternation in the optical activity of the menthyl esters but also the disappearance of alternation in solutions of the sodium salts, because in the ionised condition the electrically charged terminal groups would mutually repel one another, thus preventing association.

A second form of association may be deduced from the success of Kendall and Booge (*J. Amer. Chem. Soc.*, 1916, **38**, 1712) in isolating a large number of bimolecular addition compounds resulting from the union of acids and esters, as a consequence of which the authors conclude that complex formation of this type is a general phenomenon in systems ester–acid. The menthyl esters under discussion, being both acids and esters, may therefore exist partly in a bimolecular state due to the carboxyl of one molecule linking up with the ester group of a second. Association may also take the more complete form shown in the annexed formula, in which co-ordination is represented by the symbol adopted by Sidgwick. In the latter case, the zig-zag arrangement of the carbon chain would be expected to facilitate combination in the odd, as compared with the even series, since the odd members have a natural tendency to occur in the *cis*-structure. This would then lead to an alternation in properties. It might even be anticipated that the odd members,

existing in the cyclic bimolecular form to a greater degree than the even members, would on this account exhibit a higher rotation.



As there is no evidence pointing to an association of this type with ionised carboxyl groups, the alternation would probably not be found in the sodium salts.

Although the available data do not permit of an unequivocal decision as to the actual nature of the addition compounds formed, the assumption that the ester-acids are partly associated accounts for the observed influence of the growing chain. The alternating curves would then represent alternation due to the two types of association superimposed on the normal effect of the spiral chain.

EXPERIMENTAL.

l-*Menthyl Esters of Alkyloxyacetic Acids*.—The menthol used in the following preparations had a rotation of $[\alpha]_D^{15^\circ} = -49{\cdot}73^\circ$ in alcohol ($c = 9{\cdot}87$).

l-*Menthyl* n-*propoxyacetate*. To a boiliug solution of sodium (25 g.) in *n*-propyl alcohol (240 g.), chloroacetic acid (46 g.) was gradually added with continuous shaking. A vigorous reaction occurred and sodium chloride was deposited from the solution. After 2 hours' further heating, the yellowish product was cooled, water added, and any excess of propyl alcohol extracted from the solution with ether. The aqueous layer, evaporated to a convenient bulk, was treated with the theoretical quantity of 25% sulphuric acid; ether then extracted the propoxyacetic acid which, after heing dried, was distilled in a vacuum (yield, 37 g.); b. p. 108°/10 mm. (Gautier, *Ann. Chim.*, 1909, **16**, 309, quotes 213—214°/724 mm.) (Found: *M*, by titration, 117·5. Calc.: *M*, 118·1).

21 G. of *n*-propoxyacetyl chloride (b. p. 87—88°/101 mm.; obtained by use of thionyl chloride) were heated with menthol (24 g.), benzene (50 g.), and pyridine (2 mols.) for 4 hours on the water-bath, and the mixture was then worked up in the usual way, any unchanged menthol being distilled in steam. The l-*menthyl propoxyacetate* boiled at 161°/14 mm. and showed a constant rotatory power after one fractionation (Found: C, 70·2; H, 11·1. $C_{15}H_{28}O_3$ requires C, 70·3; H, 10·9%).

In preparing the remaining esters of this series a modification of the above procedure was adopted, anhydrous sodium chloro-

acetate (Kastle and Keiser, *Amer. Chem. J.*, 1893, **15**, 472) being used in place of chloroacetic acid. This had the advantage of requiring only half the amount of metallic sodium, thus reducing the volume of the alcohol necessary for its solution as alkyloxide.

n-*Butoxyacetic acid* was prepared from *n*-butyl alcohol (75 g.), *sodium* (8 g.), and *sodium monochloroacetate* (36 g.). Yield, 36 g. (84% theory), b. p. 115—116°/10 mm. (Found: C, 54·4; H, 9·2. $C_6H_{12}O_3$ requires C, 54·5; H, 9·15%).

l-*Menthyl* n-*butoxyacetate*. The above acid was converted into the acid chloride, and the fraction (29 g.) of this having b. p. 108—110°/108 mm. was brought into reaction with menthol in the manner described under the propoxy-ester, giving 42·5 g. of pure menthyl butoxyacetate, b. p. 172·5°/14 mm. (Found: C, 70·9; H, 11·3. $C_{16}H_{30}O_3$ requires C, 71·1; H, 11·2%).

n-*Amyloxyacetic acid*. *n*-Amyl alcohol was prepared from *n*-butyl alcohol, by converting the latter first into the bromide and thence by way of the cyanide into ethyl *n*-valerate. The latter was then reduced to *n*-amyl alcohol by means of anhydrous alcohol and sodium (Adams and Marvel, *J. Amer. Chem. Soc.*, 1920, **42**, 310). Amyl alcohol, b. p. 138—139°, was obtained in 63% yield. This was converted into n-*amyloxyacetic acid* by interaction with sodium and sodium chloroacetate (see above), the temperature of the oil bath not being allowed to exceed 130°. Reaction was complete in 3 hours. The acid boiled at 134°/12 mm. Yield, 77% (calculated on amyl alcohol) (Found: C, 57·4; H, 9·8. $C_7H_{14}O_3$ requires C, 57·5; H, 9·65%).

n-*Amyloxyacetyl chloride*, b. p. 103°/64 mm., was esterified in the usual manner to give l-*menthyl* n-*amyloxyacetate*, b. p. 148°/14 mm., the rotation of which remained constant after a second fractionation (Found: C, 71·6; H, 11·4. $C_{17}H_{32}O_3$ requires C, 71·7; H, 11·4%).

n-*Hexyloxyacetic acid*, b. p. 143—144°/10 mm., was prepared in a similar manner to the previous acids, from *n*-hexyl alcohol (Kahlbaum, b. p. 157°) (Found: C, 59·9; H, 10·1. $C_8H_{16}O_3$ requires C, 60·0; H, 10·1%).

n-*Hexyloxyacetyl chloride*, b. p. 106—108°/22 mm., was converted into l-*menthyl* n-*hexyloxyacetate*, b. p. 187°/10 mm., the rotation of which remained constant after the second fractionation (Found: C, 72·3; H, 11·6. $C_{18}H_{34}O_3$ requires C, 72·4; H, 11·5%).

n-*Heptyloxyacetic acid* (from Kahlbaum's *n*-heptyl alcohol, b. p. 175°) was a colourless liquid, b. p. 156°/10 mm., which solidified (m. p. 7·5—8·5°) in a freezing mixture (Found: C, 61·9; H, 10·5. $C_9H_{18}O_3$ requires C, 62·0; H, 10·4%).

n-*Heptyloxyacetyl chloride*, b. p. 116°/16 mm., was converted into l-*menthyl* n-*heptyloxyacetate* in the usual way. The ester was obtained

as a colourless, odourless liquid, b. p. 200°/11 mm. The rotatory power was unaltered after the second fractionation and was not affected by refluxing the ester in an air stream under diminished pressure for 30 minutes (Found: C, 73·0; H, 11·8. $C_{19}H_{36}O_3$ requires C, 73·0; H, 11·6%).

n-*Octyloxyacetic acid* was prepared from a fraction of *n*-octyl alcohol (Kahlbaum) boiling at 195·5—196°, which was optically inactive. The procedure was the same as that adopted in the case of the foregoing acids, but special care was taken to keep the temperature below 130° during the addition of the sodium chloroacetate to the sodium octyloxide dissolved in octyl alcohol. At higher temperatures, the yield of crude acid diminished and the pure product could only be obtained after wasteful fractionation. From *n*-octyl alcohol (75 g.), sodium (8 g.), and sodium chloroacetate (39 g.) there was obtained a 68% yield of n-*octyloxyacetic acid* (43 g.), b. p. 166°/10 mm. The acid solidified on standing and then melted at 12·5—13·5° (Found: C, 63·7; H, 10·7. $C_{10}H_{20}O_3$ requires C, 63·8; H, 10·7%).

n-*Octyloxyacetyl chloride*, b. p. 125—126°/12 mm., was converted into l-*menthyl* n-*octyloxyacetate*, b. p. 183°/2 mm. The rotatory power was constant after a third fractionation (Found: C, 73·5; H, 11·9. $C_{20}H_{38}O_3$ requires C, 73·6; H, 11·7%).

l-*Menthyl Hydrogen Esters of the Saturated Dicarboxylic Acids.*—In most cases the dicarboxylic acids, purified by repeated recrystallisation from a suitable solvent, were first converted into the dimenthyl esters by the method of Hilditch (J., 1909, **95**, 1571; see also Hall, J., 1923, **123**, 109). The di-ester was then submitted to half-hydrolysis at room temperature by treatment with the requisite amount of sodium dissolved in 95% alcohol. The crude acid ester was dissolved in a slight excess of dilute sodium carbonate solution and extracted repeatedly (10 times) with an equal bulk of ether, to remove menthol and di-ester. The aqueous layer was then acidified, the liberated ester-acid extracted with ether, and the extract washed (10 times) with large volumes of water to remove any dicarboxylic acid or ethyl hydrogen carboxylate which might have been formed during the half-hydrolysis. The ethereal solution, after drying over calcium chloride, gave the menthyl hydrogen ester, which was further dried in a vacuum desiccator at 55° over calcium chloride. After 16—20 hours' drying, the rotation of the ester underwent no further change. The whole of the above treatment was repeated until the rotation was unaffected by continued washings.

l-*Menthyl hydrogen glutarate* was obtained from dimethyl glutarate having a rotatory power $[\alpha]_{5461} = -84·15°$ in chloroform solution ($c = 5$). Hall (*loc. cit.*) records $[\alpha]_{5461} = -84·12°$. The rotation

of the homogeneous half-ester prepared by half-hydrolysis and washed as above was increased by 0·09° (l = 0·5) by a repetition of the process. Further washings led to no change in rotatory power. The colourless, odourless syrup gave C, 66·7; H, 9·8 ($C_{15}H_{26}O_4$ requires C, 66·6; H, 9·7%).

l-*Menthyl hydrogen adipate* was prepared from dimethyl adipate (m. p. 62·5—63·5°; $[\alpha]_{5461}$ = − 81·63° in chloroform, c = 5. Hall, *loc. cit.*, records $[\alpha]_{5461}$ = − 81·75°). Two separate preparations of the half-ester gave crude products which exhibited the same constant rotatory power after four treatments as above. The colourless, odourless syrup gave C, 67·4; H, 10·0 ($C_{16}H_{28}O_4$ requires C, 67·6; H, 9·9%).

l-*Menthyl hydrogen pimelate.* Pimelic acid, m. p. 101—103°, prepared by Perkin's method (J., 1887, **51**, 240; 1891, **59**, 822) by way of ethyl pentanetetracarboxylate was used without further purification. It gave crude dimenthyl pimelate, which was distilled in a high vacuum (b. p. 230°/0·07 mm.) and recrystallised from alcohol. The di-ester had the rotatory power $[\alpha]_{5461}$ = − 93·20° in chloroform (c = 5). Hall (*loc. cit.*) records $[\alpha]_{5461}$ = − 92·10°. l-*Menthyl hydrogen pimelate* was obtained from the di-ester in the usual manner, as a slightly yellow syrup (Found: C, 68·2; H, 10·2. $C_{17}H_{30}O_4$ requires C, 68·4; H, 10·1%).

l-*Menthyl hydrogen suberate.* Suberic acid, purified by repeated recrystallisation from ethyl acetate, was converted into dimenthyl suberate. The crude di-ester was distilled in a high vacuum (b. p. 233°/0·07 mm.) and then recrystallised from alcohol. The pure ester melted at 36·5—37·5° and gave $[\alpha]_{5461}$ = − 90·20° in chloroform (c = 5). Hall (*loc. cit.*) records m. p. 36—37° and $[\alpha]_{5461}$ = − 89·33°. l-*Menthyl hydrogen suberate*, as obtained from the di-ester, was a faintly yellow syrup (Found: C, 69·0; H, 10·6. $C_{18}H_{32}O_4$ requires C, 69·2; H, 10·3%).

l-*Menthyl hydrogen azelate.* Purified azelaic acid (m. p. 107—108°, corr.) was converted into the dimenthyl ester, which on repeated fractionation under 2 mm. pressure (b. p. 265°) had a low rotatory power. It was purified by solution in warm methyl alcohol and precipitation at − 14°. α_{5461} = − 76·42° (l = 1) for the homogeneous ester. Hall (*loc. cit.*) records α_{5461} = − 76·24°. l-*Menthyl hydrogen azelate* was obtained as a colourless syrup (Found: C, 69·7; H, 10·7. $C_{19}H_{34}O_4$ requires C, 69·9; H, 10·5%).

l-*Menthyl hydrogen sebacate*, from sebacic acid (m. p. 132·8—133·4°, corr.) was fractionated under 0·25 mm. pressure (b. p. 273°). The ester was finally purified from methyl alcohol (see azelate). α_{5461} = − 72·68° (l = 1). Hall (*loc. cit.*) records α_{5461} = − 73·12° (Found: C, 70·4; H, 10·8. $C_{20}H_{36}O_4$ requires C, 70·5; H, 10·7%).

l-Menthyl hydrogen succinate (Arth, *Ann. Chim. Phys.*, 1886, **7**, 483) and *l*-menthyl hydrogen malonate (Rule and Smith, J., 1925, **127**, 2188) were also prepared in order to obtain comparative rotations for the sodium salts in water and alcohol and for the esters in certain solvents. The succinate gave $[\alpha]_D = -70{\cdot}2°$ in benzene ($c = 5$). Pickard and Kenyon (J., 1915, **107**, 52) record $[\alpha]_D = -70{\cdot}5°$.

Observed Rotations and Densities of the Homogeneous Esters.

The sign of all the following *l*-menthyl esters is negative. Density determinations were made in a pyknometer holding about 3 c.c.

l-*Menthyl* n-*propoxyacetate* ($l = 1$).

$D_{4°}^{t°}$ 0·9448 at 24°; 0·9286 at 44·2°; 0·9151 at 61·05°; 0·8999 at 79·5°.
α_{6708} 44·42° at 18°; 44·04° at 37·5°; 43·36° at 65·1°; 42·64° at 93·1°.
α_{5893} 58·69° at 18°; 58·16° at 39·1°; 57·08° at 71·9°; 56·37° at 92·0°.
α_{5780} 61·31° at 18°; 60·63° at 39·1°; 59·49° at 71·9°; 58·73° at 92·0°.
α_{5461} 69·44° at 18°; 68·62° at 39·1°; 67·36° at 71·9°; 66·51° at 92·0°.
α_{4358} 115·49° at 18°; 114·26° at 39·1°; 111·95° at 71·9°; 110·49° at 92·0°.

l-*Menthyl* n-*butoxyacetate* ($l = 1$).

$D_{4°}^{t°}$ 0·9397 at 20·6°; 0·9228 at 42·2°; 0·9094 at 59·4°; 0·8932 at 80·1°.
α_{6708} 42·34° at 20·5°; 41·82° at 40·6°; 41·07° at 66·2°; 40·29° at 91·5°.
α_{5893} 55·74° at 20·5°; 55·08° at 40·6°; 54·17° at 66·2°; 53·15° at 91·5°.
α_{5780} 58·14° at 20·5°; 57·51° at 40·6°; 56·54° at 66·2°; 55·50° at 91·5°.
α_{5461} 65·83° at 20·5°; 65·13° at 40·6°; 64·08° at 66·2°; 62·91° at 91·5°.
α_{4358} 109·43° at 20·5°; 108·28° at 40·6°; 106·51° at 66·2°; 104·58° at 91·5°.

l-*Menthyl* n-*amyloxyacetate* ($l = 1$).

$D_{4°}^{t°}$ 0·9340 at 20·5°; 0·9174 at 42·5°; 0·9055 at 58·3°; 0·8864 at 83·5°.
α_{6708} 39·83° at 21·5°; 39·41° at 39°; 38·65° at 67°; 37·93° at 89·7°.
α_{5893} 52·52° at 21·5°; 51·93° at 39°; 51·0° at 67°; 50·11° at 89·7°.
α_{5780} 54·80° at 21·5°; 54·25° at 39°; 53·18° at 67°; 52·32° at 89·7°.
α_{5461} 61·99° at 21·5°; 61·44° at 39°; 60·26° at 67°; 59·28° at 89·7°.
α_{4358} 103·12° at 21·5°; 102·0° at 39°; 100·3° at 67°; 98·61° at 89·7°.

l-*Menthyl* n-*hexyloxyacetate* ($l = 1$).

$D_{4°}^{t°}$ 0·9270 at 24·3°; 0·9125 at 43·9°; 0·8985 at 62·7°; 0·8865 at 79·3°.
α_{6708} 37·31° at 21°; 36·96° at 38·1°; 36·19° at 65°; 35·40° at 94·5°.
α_{5893} 49·29° at 21°; 48·77° at 38·1°; 47·88° at 65°; 46·78° at 94·5°.
α_{5780} 51·33° at 21°; 50·84° at 38·1°; 49·90° at 65°; 48·83° at 94·5°.
α_{5461} 58·25° at 21°; 57·62° at 38·1°; 56·57° at 65°; 55·32° at 94·5°.
α_{4358} 96·82° at 21°; 95·74° at 38·1°; 94·18° at 65°; 92·05° at 94·5°.

l-*Menthyl* n-*heptyloxyacetate* ($l = 1$).

$D_{4°}^{t°}$ 0·9221 at 24·5°; 0·9101 at 40·9°; 0·8962 at 59·9°; 0·8818 at 79·7°.
α_{6708} 35·29° at 22°; 35·05° at 39·5°; 34·47° at 64·3°; 33·88° at 87·1°.
α_{5893} 46·74° at 22°; 46·24° at 39·5°; 45·50° at 64·3°; 44·74° at 87·1°.
α_{5780} 48·66° at 22°; 48·20° at 39·5°; 47·52° at 64·3°; 46·73° at 87·1°.
α_{5461} 55·11° at 22°; 54·54° at 39·5°; 53·61° at 64·3°; 52·89° at 87·1°.
α_{4358} 91·76° at 22°; 90·86° at 39·5°; 89·41° at 64·3°; 87·95° at 87·1°.

l-*Menthyl* n-*octyloxyacetate* ($l = 1$).

$D_{4°}^{t°}$ 0·9214 at 20·8°; 0·9072 at 40·1°; 0·8932 at 59·1°; 0·8779 at 79·9°.
α_{6708} 33·86° at 17·8°; 33·44° at 39°; 32·78° at 70·2°; 32·30° at 91·2°.
α_{5893} 44·64° at 17·8°; 44·07° at 39°; 43·23° at 70·2°; 42·57° at 91·2°.
α_{5780} 46·54° at 17·8°; 46·05° at 39°; 45·02° at 70·2°; 44·42° at 91·2°.
α_{5461} 52·69° at 17·8°; 52·08° at 39°; 51·03° at 70·2°; 50·28° at 91·2°.
α_{4358} 87·64° at 17·8°; 86·49° at 39°; 84·82° at 70·2°; 83·65° at 91·2°.

l-Menthyl hydrogen malonate.

Solvent.	*l.*	*t.*	G. ester/ 20 c.c.	α_{6708}.	α_{5893}.	α_{5780}.	α_{5461}.	α_{4358}.
EtOH	200	20°	0·8127	—	—	—	6·55°	10·87°
$CHCl_3$	200	20·4	1·0146	5·49°	7·22°	7·52°	8·52	14·16
Sod. salt } H_2O...	200	20·2	1·0007	5·16	6·84	7·16	8·07	13·44
l-Menthyl hydrogen succinate.								
Sod. salt } H_2O...	200	15	0·9302	—	—	—	7·04	—
l-Menthyl hydrogen glutarate.								
Homog. ...	50	21·0	(*d* 1·0318)	23·49	31·02	32·34	36·03	60·79
Homog. ...	50	60·2	(*d* 1·0046)	22·81	30·05	31·35	35·52	58·93
$CHCl_3$	200	18·9	1·0278	5·00	6·58	6·85	7·73	12·84
EtOH	200	19·5	1·0098	4·82	6·33	6·64	7·48	12·47
C_6H_6	200	19·5	1·0246	4·86	6·38	6·65	7·52	12·52
Sod. } H_2O...	200	18·0	*1·0389	4·71	6·17	6·45	7·29	12·12
salt } EtOH	200	15·0	*0·8697	—	—	—	6·38	—
l-Menthyl hydrogen adipate.								
Homog. ...	50	20·0	(*d* 1·0252)	21·50	28·36	29·52	33·47	55·54
Homog. ...	50	60·0	(*d* 0·9959)	20·75	27·38	28·58	32·40	53·67
$CHCl_3$	200	18·4	1·0383	4·64	6·17	6·44	7·27	12·06
EtOH	200	19·2	1·0539	4·65	6·15	6·39	7·25	12·02
C_6H_6	200	18·3	1·0793	4·70	6·22	6·47	7·33	12·13
Sod. } H_2O...	200	19·5	1·0125	4·27	5·61	5·88	6·64	11·06
salt } EtOH	200	16·0	0·7544	—	—	—	5·23	—
l-Menthyl hydrogen pimelate.								
Homog. ...	50	19·0	(*d* 1·0141)	20·45	26·89	28·00	31·73	—
Homog. ...	50	59·0	(*d* 0·9858)	19·65	25·93	27·03	30·63	—
$CHCl_3$	200	18·5	0·9835	4·21	5·56	5·80	6·54	10·89
EtOH	200	19·0	1·0320	4·37	5·78	6·05	6·88	11·36
C_6H_6	200	18·0	1·0418	4·35	5·70	5·94	6·71	11·10
Sod. } H_2O...	200	19·0	1·0060	3·98	5·24	5·48	6·19	10·21
salt } EtOH	100	15·0	0·7590	—	—	—	2·51	—
l-Menthyl hydrogen suberate.								
Homog. ...	50	19·2	(*d* 1·0049)	18·83	24·86	25·98	29·45	—
Homog. ...	50	60·3	(*d* 0·9760)	18·18	24·04	25·03	28·38	—
$CHCl_3$	200	19·0	0·9828	3·95	5·21	5·46	6·18	10·26
EtOH	200	18·8	0·9668	3·85	5·07	5·31	6·01	9·96
C_6H_6	200	20·0	1·0306	3·97	5·27	5·50	6·22	10·36
Sod. } H_2O...	200	19·0	1·0672	3·89	5·14	5·35	6·03	10·02
salt } EtOH	200	16·0	0·8707	—	—	—	5·53	—

l-Menthyl hydrogen azelate.

Solvent.	*l.*	*t.*	G. ester/ 10 c.c.	α_{5893}.	α_{5461}.	α_{4358}.
Homog.	50	20°	(*d* 0·9952)	23·64°	28·63°	47·69°
C_6H_6	100	20	0·5733	2·98	3·47	5·60
EtOH	100	20	0·5368	2·81	3·29	5·37
Sod. } H_2O......	100	20	0·4596	—	2·39	3·93
salt } EtOH ...	100	20	0·4667	—	2·85	—
l-Menthyl hydrogen sebacate.						
Homog.	50	20	(*d* 0·9923)	23·13	27·37	45·28
C_6H_6	100	20	0·5275	2·51	3·03	4·89
EtOH	100	20	0·4457	2·12	2·61	4·24
Sod. } H_2O......	100	20	0·4309	—	2·27	3·62
salt } EtOH ...	100	20	0·3894	—	2·12	—

* Rotations with the sodium salts were made by dissolving a weighed amount of ester in water or alcohol, and adding the calculated quantity of alkali dissolved in the same solvent.

Summary.

1. The rotatory powers of a number of the homologous menthy alkyloxyacetic esters and menthyl hydrogen dicarboxylic esters have been investigated. It is found that the maxima in the rotation curves of the one series correspond to minima in the other. This indicates that the terminal alkyloxyl and carboxyl groups of the growing chains produce opposite changes in rotatory power when they return to the neighbourhood of the asymmetric atom. Similar effects are noted in the influence of substituents on the acidity of geometrically isomeric acids. Hence it is concluded that the characteristic influence of *o*-substituents in the optically active benzoic esters (Rule, Hay, Numbers, and Paterson, this vol., p. 178) is propagated through space.

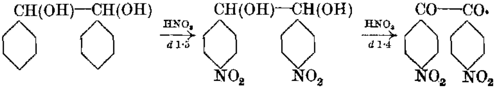
2. The rotatory powers of the menthyl hydrogen dicarboxylates exhibit pronounced alternation, both in the homogeneous state and in solution. This alternation disappears in the sodium salts. It is suggested that the alternation is a superimposed secondary effect due to association of the ester-acids through the medium of the carboxyl groups.

UNIVERSITY OF EDINBURGH. [*Received, March 14th*, 1928.]

CLXXXI.—*The Preparation of* 4 : 4′-*Dinitrobenzil.*

By FREDERICK DANIEL CHATTAWAY and EDWARD AUTY COULSON.

WHEN hydrobenzoin is nitrated with fuming nitric acid at a low temperature and the product oxidised by boiling with concentrated nitric acid, 4 : 4′-dinitrobenzil is produced in considerable quantity, *the group ·CH(OH)·, as in benzoin, exerting a strong para-directing* influence on the nitro-group entering the nucleus to which it is attached :-



4 : 4′-Dinitrobenzil forms derivatives similar to those obtained from the other five isomeric heteronuclear dinitrobenzils. On oxidation by chromic acid it yields an approximately theoretical amount of *p*-nitrobenzoic acid, a reaction which establishes its constitution.

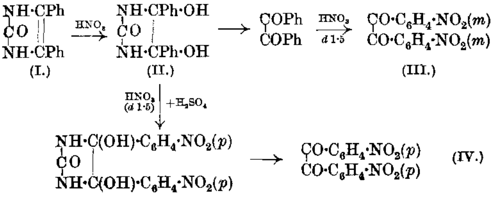
It proves to be identical with the compound obtained by Biltz

(*Annalen*, 1909, **368**, 262, footnote) by the nitration of 4 : 5-diphenylglyoxalone (I). Analysis showed the nitration product to have the composition of a dinitrobenzil and it was assumed to have the 4 : 4′-configuration, though this was not established.

As the preparation of hydrobenzoin is a troublesome operation, whereas 4 : 5-diphenylglyoxalone is very easily made by heating together benzoin and urea in acetic acid solution, the latter componnd affords a convenient starting material for the production of 4 : 4′-dinitrobenzil (IV) in quantity, as from it approximately a quarter of its weight of pure 4 : 4′-dinitrobenzil can be obtained. The nitration must be effected by a mixture of concentrated sulphuric and fuming nitric acids; if fuming nitric acid alone is used, the products are only those obtained when benzil itself is nitrated.

Biltz (*Annalen*, 1909, **368**, 165) found that 4 : 5-diphenylglyoxalone was very easily oxidised by cold dilute nitric acid to 4 : 5-dihydroxy-4 : 5-diphenyldihydroglyoxalone (II), which rapidly broke down into benzil and urea. It is probably in this glycol (II) only that substitution in the two para-positions occurs, the group ·C(OH)·NH>CO / ·C(OH)·NH exerting a directing influence similar to that of the ·CH(OH)·CH(OH)· group in hydrobenzoin, the 3 : 3′-dinitrobenzil (III) always formed at the same time, and to the exclusion of the 4 : 4′-isomeride if fuming nitric acid alone is used, being produced by the action of the nitric acid on the liberated benzil.

The 2 : 3′- and the 2 : 2′-isomerides are almost certainly present in the residue left after the isolation of the 4 : 4′-dinitrobenzil, but as the complete separation of such a mixture is extraordinarily tedious, it has not been exhaustively worked up. The reactions may be represented by the following scheme :



Experimental.

Interaction of Hydrobenzoin with Fuming Nitric Acid.—2·5 G. of hydrobenzoin, m. p. 132° (Breuer and Zincke, *Annalen*, 1879, **198**,

151, 153), were gradually added to 15 c.c. of nitric acid (*d* 1·5) at −10° to −5°. The temperature was then allowed to rise to 0° and after 2 hours the reaction mixture was diluted with 7 c.c. of water, boiled for ½ hour in order completely to oxidise the nitration product to the corresponding dinitrobenzil, and poured on ice. The semi-solid mass which separated was removed, boiled with water, and drained as completely as possible. It then solidified and after one crystallisation from acetone a product, m. p. 197—212°, was obtained; a second crystallisation raised the m. p. to 213° (constant) (yield, 1 g.). The acetone mother-liquors deposited a small amount of a friable semi-crystalline powder which was not further examined.

Oxidation of 4 : 4'-*Dinitrobenzil* (IV).—4 : 4'-Dinitrobenzil is slightly more soluble in all solvents than the 2 : 2'-isomeride but less soluble than the others. It is sparingly soluble in boiling alcohol, but fairly soluble in acetone and acetic acid and crystallises from the latter in very large, yellow, irregularly grown, elongated plates, m. p. 213° (Found : N, 9·3. Calc. for $C_{14}H_8O_6N_2$: N, 9·3%).

6·5 G. of 4 : 4'-dinitrobenzil were boiled for a short time with a slight excess of chromic acid anhydride in acetic acid and after concentration the solution was treated with a slight excess of dilute soda solution and filtered. On acidification, 0·63 g. of *p*-nitrobenzoic acid, m. p. 237°, was obtained (mixed m. p. with an authentic sample showing no depression). Yield, 87% of the theoretical.

4 : 4'-*Dinitrobenzilmonophenylhydrazone* separated when equivalent amounts of the diketone and phenylhydrazine were boiled together for a few minutes in alcoholic solution. It crystallised from acetic acid, in which it is moderately easily soluble, in very fine, hair-like, deep orange crystals, m. p. 257° (Found : N, 14·5. $C_{20}H_{14}O_5N_4$ requires N, 14·4%).

4 : 4'-*Dinitrobenzilosazone* is produced slowly and in poor yield when the diketone is boiled with phenylhydrazine in acetic acid solution, but by taking excess of phenylhydrazine and adding phosphoric oxide the formation of the osazone is greatly facilitated. It is sparingly soluble in all solvents and crystallises from acetic anhydride in tufts of small, red plates, m. p. 293° (decomp.) (Found : N, 17·3. $C_{26}H_{20}O_4N_6$ requires N, 17·5%).

2 : 3-*Di*-p-*nitrophenylquinoxaline* is very soluble in boiling acetic acid and crystallises in colourless needles, m. p. 201° (Found : N, 14·9. $C_{20}H_{12}O_4N_4$ requires N, 15·1%).

Preparation of 4 : 5-*Diphenylglyoxalone*.—Of the various methods for the preparation of this compound the best is that of Biltz (*Annalen*, 1909, **368**, 173). 50 G. of benzoin were boiled under reflux with 26 g. of urea in 200 g. of acetic acid for 6 hours. The glyoxalone crystallised from the reaction mixture on cooling and was

filtered off, washed with cold acetic acid, ether, and, lastly, with boiling water, and crystallised from acetic acid. It formed colourless needles, m. p. 324° (yield, 40 g.).

Interaction of 4 : 5-*Diphenylglyoxalone with Fuming Nitric Acid.*—10 G. of 4 : 5-diphenylglyoxalone were dissolved in 20 g. of nitric acid (*d* 1·5), cooled to 0°. The solution was kept over-night and then poured into water. The yellow semi-solid mass obtained was well washed with hot water and recrystallised from acetone, 4 g. of pure 3 : 3′-dinitrobenzil, m. p. 132°, being isolated. No formation of 4 : 4′-dinitrobenzil was observed.

Interaction of 4 : 5-*Diphenylglyoxalone with Sulphuric and Fuming Nitric Acids.*—27 G. of 4 : 5-diphenylglyoxalone were dissolved in 315 g. of concentrated sulphuric acid cooled to −5° and 90 g. of nitric acid (*d* 1·5) were slowly added, the temperature being kept below 0° during the addition. The reaction mixture was kept at the ordinary temperature for 3 days; considerable effervescence took place and a flocculent, yellow mass separated from the solution. The whole was then poured on ice and the yellow, semi-solid mass was removed, boiled repeatedly with water, and drained as completely as possible. After three crystallisations from acetic acid the product yielded 7 g. of pure 4 : 4′-dinitrobenzil, m. p. 213°, identical with a specimen made from hydrobenzoin.

The acetic acid mother-liquors slowly deposited a yellow, moss-like mass of crystals, which were removed and crystallised four times from acetone, 10 g. of pure 3 : 3′-dinitrobenzil, m. p. 132°, being obtained (identical with a specimen made from benzil; compare J., 1926, 1070).

THE QUEEN'S COLLEGE, OXFORD. [*Received, March 9th,* 1928.]

CLXXXII.—*The Nitration of Aromatic Thiocyanates and Selenocyanates.*

By FREDERICK CHALLENGER and ARNOLD THORNTON PETERS.

IN a previous communication by one of us and Collins (J., 1924, **125**, 1377) it was shown by the nitration of phenyl thiocyanate that the thiocyano-group possesses a strong para-directing influence, relatively very small amounts of *o*-nitrophenyl thiocyanate being formed. When the para-position is occupied by (*a*) chlorine or (*b*) bromine, the nitro-group enters in the ortho-position to ·SCN. In case (*a*), the product was homogeneous, whereas in (*b*) traces of a second nitro-compound appeared to be present. With *p*-iodophenyl thiocyanate and *p*-bromoiodobenzene replacement of iodine by the

nitro-group occurs. Mayes and Turner (this vol., p. 691) have observed a similar effect.

On nitration of *p*-tolyl thiocyanate, however, two isomeric mono-nitro-compounds are formed, the principal product containing the nitro-group in the ortho-position to methyl. In this case, the course of the reaction appears to be determined chiefly by the methyl group.

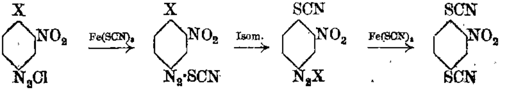
It was therefore of interest to ascertain the behaviour of *o*-tolyl thiocyanate (Thurnauer, *Ber.*, 1890, **23**, 771) on nitration, and it has now been shown that the principal product is *5-nitro-*o*-tolyl thiocyanate* and a much smaller amount of the *4-nitro*-derivative is produced. The influence of the thiocyano-group is therefore predominant. Here, as in all other cases described in this communication, the products of nitration were identified by direct comparison with authentic thiocyanates or selenocyanates obtained by the diazo-reaction.

In a later communication, it is hoped to discuss more fully the differing behaviour of the *o*- and *p*-tolyl thiocyanates, and Miss C. Higginbottom, B.Sc., is, in this connexion, studying the nitration of the *o*-halogenophenyl thiocyanates.

When 4-bromo (or chloro)-3-nitroaniline is diazotised and treated with ferric thiocyanate or with potassium cuprous thiocyanate, *4-bromo-3-nitrophenyl thiocyanate* and *4-chloro-3-nitrophenyl thiocyanate* are obtained. A large quantity of *nitro-*p*-dithiocyanobenzene* is also produced in each case, a halogen atom being eliminated. This has been identified by direct comparison with the product obtained (1) by nitration of the *p*-dithiocyanate and (2) from diazotised 2-nitro-4-thiocyanoaniline.

It was shown by Hantzsch and Hirsch (*Ber.*, 1896, **29**, 947; 1898, **31**, 1253) that the *p*-chloro- and *p*-bromo-benzenediazonium thiocyanates readily isomerise, usually in presence of acid, giving the *p*-thiocyanobenzenediazonium chloride or bromide. Similarly, 2 : 4-dibromobenzenediazonium chloride gives rise to a mixture of chlorobromo- and dichloro-benzenediazonium bromides (Hantzsch, *Ber.*, 1897, **30**, 2334).

The replacement of chlorine or bromine by thiocyanogen with production of a nitrodithiocyanobenzene probably proceeds in an analogous manner.



The formation of *p*-dithiocyanobenzene has not yet been observed

during the preparation of *p*-chloro- and *p*-bromo-phenyl thiocyanates, although from the work of Hantzsch and Hirsch some dithiocyanate might be expected. The abnormal course of the Sandmeyer reaction with diazotised 4-chloro (or bromo)-3-nitroaniline and a thiocyanate is probably conditioned by the reactivity of the halogen atom in presence of the *o*-nitro-group, since with 4-bromo-2-nitroaniline the reaction proceeds normally (Challenger and Collins, J., 1924, **125**, 1379).

No abnormality could be detected when 4-bromo-3-nitroaniline was diazotised and treated with cuprous chloride, the sole product of the reaction apart from a trace of a high-melting solid being 4-chloro-1-bromo-2-nitrobenzene, m. p. 69—70° (Holleman, *Rec. trav. chim.*, 1915, **34**, 208, gives m. p. 70°). Nitro-*p*-dichlorobenzene could not be detected.

2-Nitro-4-thiocyanoaniline was obtained by nitration of *p*-thiocyanoacetanilide prepared by acetylation of the corresponding amine (Soderbäck, *Annalen*, 1919, **419**, 271). Its structure was proved by diazotisation and elimination of the diazo-group giving *m*-nitrophenyl thiocyanate. Replacement of the amino-gronp by chlorine, bromine, or selenocyanogen gives 4-*chloro*-3-*nitrophenyl thiocyanate*, 4-*bromo*-3-*nitrophenyl thiocyanate*, and 3-*nitro*-4-*selenocyanophenyl thiocyanate*, which were required as reference compounds for orientation purposes. p-*Dithiocyanobenzene* and p-*thiocyanoselenocyanobenzene* have been prepared from diazotised *p*-thiocyanoaniline.

The orienting effect of the selenocyano-group has also been investigated. *Phenyl selenocyanate*, which has not previously been described, gives on nitration principally the para-derivative, but some *o*-nitrophenyl selenocyanate is also obtained.

A comparison of the relative orienting effects of SeCN and the halogens and of SeCN and SCN has been attempted. This has, however, only been partly successful, since in many cases, even under the most varied conditions, the nitration of halogenated phenyl selenocyanates and of thiocyanoselenocyanobenzene leads to the production of aromatic seleninic acids, $R{\cdot}SeO_2H$, some of which have recently been obtained by Porritt (J., 1927, 27), using a different method. The nitration of *p*-tolyl selenocyanate (Challenger, Peters, and Halévy, J., 1926, 1654) with nitric acid (*d* 1·5) at −10° proceeds normally, giving as principal product 2-*nitro*-p-*tolyl thiocyanate*, m. p. 69°, the isomeric 3-*nitro*-derivative, m. p. 150°, being obtained in much smaller amount. This recalls the nitration of *p*-tolyl thiocyanate where the lower-melting 2-nitro-derivative predominates. When the nitration is conducted with sulphuric acid and nitric acid (*d* 1·41) at 3°, a mixture of di-2-nitro-*p*-tolyl

diselenide and 2-nitro-*p*-tolueneseleninic acid is obtained. These are mutually interconvertible by oxidation and reduction. The position of the nitro-group in the diselenide was proved by its formation when synthetic 2-nitro-*p*-tolyl selenocyanate was treated with aqueous potassium hydroxide. When di-*p*-tolyl diselenide is warmed with nitric acid (*d* 1·41), *p*-tolueneseleninic acid is produced. This was obtained by Porritt by the oxidation of *p*-tolylselenoglycollic acid, $CH_3{\cdot}C_6H_4{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$, with hydrogen peroxide.

When *p*-chlorophenyl selenocyanate is nitrated with nitric (*d* 1·41), and sulphuric acids below 3°, a mixture of di-*p*-chlorophenyl diselenide (Taboury, *Bull. Soc. chim.*, 1906, **35**, 673) and *p*-chlorobenzeneseleninic acid (Porritt, *loc. cit.*; Morgan and Elliot, P., 1914, 248) is produced. With nitric acid (*d* 1·5) at −25° or −10°, a mixture of the seleninic acid and of 4-*chloro*-2-*nitrophenyl selenocyanate* is obtained, the acid predominating. No trace of a derivative containing a nitro-group in position 3 could be detected. The course of the nitration is therefore again analogous to that observed with the corresponding thiocyanate. On treatment of *p*-bromophenyl selenocyanate with nitric acid under the most varied conditions, only *p*-bromobenzeneseleninic acid could be isolated (Porritt, *loc. cit.*). It was characterised by reduction to the diselenide. The crude seleninic acid gives no purple colour with alcoholic alkali, indicating the absence of even traces of 4-bromo-2-nitrophenyl selenocyanate.

Treatment of *p*-thiocyanoselenocyanobenzene with nitric acid (*d* 1·41) and sulphuric acid at 3° or with nitric acid (*d* 1·5) at −5° gives rise almost exclusively to p-*thiocyanobenezeneseleninic acid.* Traces of a second product containing sulphur, selenium, and nitrogen were once observed, but could not again be isolated.

Marsh (J., 1927, 3164) has shown that by the action of potassium thiocyanate and hydrogen peroxide on dimethylaniline in glacial acetic acid a product, m. p. 73°, is obtained which is identical with that obtained by Soderbäck (*Annalen*, 1919, **419**, 275) from an ethereal solution of thiocyanogen and dimethylaniline, and considered by him to be *p*-thiocyanodimethylaniline. Marsh suggests that this compound is probably not a true thiocyanate, bnt may have the constitution $Me_2N{\cdot}C_6H_3{<}{}^{S}_{N}{>}CH$ and be identical with the benzthiazole derivative obtained by Schmidt (*Ber.*, 1906, **39**, 2409). We find, however, that with alcoholic potassium hydrosulphide it behaves normally, giving potassium thiocyanate, and that it may be obtained by heating *p*-thiocyanoaniline with excess of methyl iodide and liberation of the base with sodium bicarbonate (m. p. and mixed m. p. with Marsh's compound, 73°). The results of one

of us and Collins (*loc. cit.*), of Dienske (*Rec. trav. chim.*, 1927, **46**, 154), and those described in this communication leave no room for doubt as to the constitution of *p*-thiocyanoaniline, which may also be obtained from aniline by Marsh's method. We have, however, prepared Schmidt's dimethylaminobenzthiazole (m. p. 73—74°) and find that it depresses the m. p. (73°) of Marsh's dimethylaniline derivative to 52°. There can therefore be no doubt that the compound obtained by Soderbäck and by Marsh is *p*-thiocyanodimethylaniline.

EXPERIMENTAL.

Nitration of o-*Tolyl Thiocyanate*.—The thiocyanate (15 g.) was slowly stirred into a mixture of nitric acid (*d* 1·41; 55 c.c.) and sulphuric acid (55 c.c.) at 3—8°, which after 3 hours was poured on ice, and the solid separated. Four crystallisations from alcohol gave white needles, m. p. 117·5—118·5°, not depressing the m. p. of 5-*nitro*-o-*tolyl thiocyanate* obtained from the corresponding nitro-*o*-toluidine by the Sandmeyer reaction. These formed the bulk of the nitration product (Found: S, 16·2. $C_8H_6O_2N_2S$ requires S, 16·5%). The mother-liquors deposited an oil which slowly solidified, and on recrystallisation white needles, m. p. 70—71°, were finally obtained. These did not depress the m. p. (70—70·5°) of 4-*nitro*-o-*tolyl thiocyanate* obtained by the Sandmeyer reaction.

Synthesis of the Isomeric Nitro-o-*tolyl Thiocyanates*.—(a) 5-*Nitro*-o-*tolyl thiocyanate*. 5-Nitro-*o*-toluidine (6 g.) in 60 c.c. of dilute sulphuric acid (1 : 5) was diazotised at 6° with 2·75 g. of sodium nitrite in 5 c.c. of water and added to a cold mixture of cuprous thiocyanate (10·8 g.) and potassium thiocyanate (5 g.) in the minimum of water. After 12 hours, the mixture was warmed at 100°; the precipitate was extracted with alcohol and after treatment with charcoal yielded colourless needles, m. p. 117·5—119°.

(b) 4-*Nitro*-o-*tolyl thiocyanate* was similarly prepared from the corresponding nitrotoluidine. It forms colourless needles, m. p. 70—70·5°, from light petroleum (Found: S, 16·2. $C_8H_6O_2N_2S$ requires S, 16·5%). The presence of the thiocyano-radical was proved by the formation of a mercaptan and potassium thiocyanate when the compound was boiled with alcoholic potassium hydrosulphide (Challenger and Collins, J., 1924, **125**, 1379).

In (a) and (b) the yields of nitro-thiocyanates are about 80%.

Preparation and Nitration of Phenyl Selenocyanate.—Aniline (9·1 g.) in dilute sulphuric acid (1 : 4) was diazotised at 3° with sodium nitrite (9·5 g.). The solution, made neutral to Congo paper with sodium acetate, was added to cold aqueous potassium selenocyanate (22 g.). The odour of an aryl selenocyanate was at once produced and after 15 hours steam distillation gave a pale yellow

oil. After being dried with calcium chloride, this boiled at 134°/10 mm. and at about 250° (decomp.) at the ordinary pressure (yield, about 50%) (Found: N, 8·0; Se, 43·0, 43·0. C_7H_5NSe requires N, 7·7; Se, 43·4%). The selenocyanate (2 g.) was dissolved in nitric acid (*d* 1·5; 7 c.c.) at −5° and after 2 hours the mixture was poured on ice. The resulting solid (2·3 g.; m. p. 105°) was fractionated from alcohol, giving white, glistening plates of *p*-nitrophenyl selenocyanate, m. p. 141°, which developed a red colour with alcoholic potassium hydroxide and did not depress the m. p. of an authentic specimen obtained from *p*-nitroaniline (Bauer, *Ber.*, 1913, **46**, 92). The final mother-liquors yielded a relatively very small amount of *o*-nitrophenyl selenocyanate, m. p. 142—143°, not depressing the m. p. of a synthetic specimen (m. p. 143°) prepared from *o*-nitroaniline. It gave a strong purple colour with alcoholic potassium hydroxide (Bauer), which we find to be characteristic of selenocyanates containing an *o*-nitro-group. Bauer (*loc. cit.*) gives the m. p.'s of the *p*- and *o*-derivatives as 135° and 142°, respectively.

Pyman (J., 1919, **115**, 166) reduced *m*-nitrophenyl selenocyanate to the diamino-diselenide without giving details of the selenocyanate. As this compound is not mentioned elsewhere in the literature, we have prepared it from *m*-nitroaniline (see p. 1374). On crystallisation from light petroleum or from acetone–light petroleum it forms almost colourless plates, m. p. 65° (Found: N, 12·25. Calc. for $C_7H_4O_2N_2Se$: N, 12·3%).

Nitration of p-*Tolyl Selenocyanate.*—The selenocyanate (9 g.) was treated with nitric acid (*d* 1·41; 30 c.c.) and sulphuric acid (32 c.c.) at 3°, and after remaining for 4 hours at room temperature the mixture was poured on ice (100 g.). The pale yellow solid (12·5 g.) obtained, on fractionation from acetone–light petroleum, gave (A) white crystals, m. p. 151°, and (B) yellow crystals, m. p. 69°, which formed the bulk of the product. (A) was faintly acid and dissolved with effervescence in sodium bicarbonate solution, from which a silver salt could be precipitated. Analysis showed (A) to be 2-*nitro*-p-*tolueneseleninic acid* (Found: Se, 32·2, 31·8. $C_7H_7O_4NSe$ requires Se, 31·9%). Reduction with zinc and hydrochloric acid gave a yellow solid, m. p. 69° (from light petroleum), not depressing the m. p. of (B) obtained as above, nor that of the synthetic *di*-2-*nitro*-p-*tolyl diselenide* (m. p. 69°) obtained by the action of potassium hydroxide on the corresponding synthetic selenocyanate prepared by the diazo-reaction (see p. 1374) (Found for the synthetic diselenide: Se, 36·7, 36·6. $C_{14}H_{12}O_4N_2Se_2$ requires Se, 36·9%).

(B) was insoluble in sodium bicarbonate solution and unaffected by aqueous alkali and was obviously di-2-nitro-*p*-tolyl diselenide.

Gentle warming with nitric acid gave (A), m. p. and mixed m. p. 151°. On treatment with equal volumes of nitric acid (*d* 1·41) and glacial acetic acid, the selenocyanate was unchanged, even after gentle warming.

Nitration unaccompanied by oxidation was effected by slowly adding the selenocyanate (3 g.) to nitric acid (*d* 1·5 ; 10 c.c.) at −10°. The solution was poured on ice (80 g.), and the precipitate (3·4 g.) crystallised from light petroleum, giving yellow needles (C), m. p. 69—70°, not depressing the m. p. of 2-*nitro*-p-*tolyl selenocyanate* obtained by the diazo-reaction ; but in admixture with (B) obtained in the previous experiment, (C) melted at 54—55° (Found : N, 11·8. $C_8H_6O_2N_2Se$ requires N, 11·6%). The petroleum mother-liquors yielded relatively small amounts of a more soluble product (D) as yellow needles, m. p. 150°, not depressing the m. p. of 3-*nitro*-p-*tolyl selenocyanate* prepared in a yield of 70% from 3-nitro-*p*-toluidine (see p. 1374) (Found : Se, 32·45. $C_8H_6O_2N_2Se$ requires Se, 32·7%). The similarity in m. p. exhibited by the entirely dissimilar pairs of compounds (A) and (D) and (B) and (C) is of interest. A mixture of nitric acid (*d* 1·41) and sulphuric acid at −10° to −15° gave similar results, a certain amount of a nitrotolueneseleninic acid being also formed. The syntheses of (C) and (D) by means of the diazo-reaction are recorded in the table on p. 1374 [Found : (for C) N, 11·9 ; Se, 32·5 ; for (D) N, 11·9. $C_8H_6O_2N_2Se$ requires N, 11·6 ; Se, 32·7%].

Nitration of p-*Chlorophenyl Selenocyanate.*—The selenocyanate (11·5 g.) was treated with nitric acid (*d* 1·41 ; 42 c.c.) and sulphuric acid (42 c.c.) below 3°. After 2 hours, ice precipitated a yellow solid (14 g.), which was separated by alcohol into orange crystals (E ; the main product), m. p. 89°, and a white solid (F), m. p. 180°. The m. p. of di-*p*-chlorophenyl diselenide (m. p. 89°), prepared from *p*-chlorophenyl selenocyanate and aqueous potassium hydroxide (Taboury, *Bull. Soc. chim.*, 1905, **35**, 673 ; Challenger, Peters, and Halévy, J., 1926, 1655), was not depressed on admixture with (E) ; and (F) was shown to be *p*-chlorobenzeneseleninic acid (Morgan and Elliott, P., 1914, **30**, 248), being soluble with effervescence in sodium bicarbonate solution and on reduction with zinc and hydrochloric acid giving the diselenide (E) (Found : Se, 35·4. Calc. for $C_6H_5O_2ClSe$: Se, 35·4%).

Similar results were obtained with sodium nitrate and sulphuric acid. Nitric acid (*d* 1·41) between −10° and 60° had no action on *p*-chlorophenyl selenocyanate. The action of equal volumes of acetic anhydride and nitric acid (*d* 1·5) at −10° gave the seleninic acid (F) and no trace of a nitro-compound.

Successful nitration was effected by treating the selenocyanate

(8 g.) with nitric acid (*d* 1·5; 25 c.c.) at $-10°$. Addition of ice after 1 hour gave a white solid (10 g.) which, when crystallised from alcohol, gave *p*-chlorobenzeneseleninic acid, m. p. 180°, and a small amount of pale yellow crystals (G), m. p. 127°, not depressing the m. p. of 2-*nitro*-p-*chlorophenyl selenocyanate* prepared by the diazo-reaction (p. 1374) (Found for this synthetic specimen: N, 10·8; Se, 29·9. $C_7H_3O_2N_2ClSe$ requires N, 10·7; Se, 30·3%). The same result was obtained at $-25°$, 0°, 15° and 50°. At the last two temperatures, only traces of the nitro-selenocyanate were obtained, recognisable by the purple colour produced with alcoholic alkali.

Nitric Acid and p-*Bromophenyl Selenocyanate*.—Nitric acid (*d* 1·5; 20 c.c.) and the selenocyanate (7 g.) were allowed to react at $-10°$, and ice (50 g.) was added after 1 hour. The almost white solid (9 g.) obtained gave no colour with alcoholic alkali, had m. p. 177°, was wholly soluble in sodium bicarbonate solution, and after crystallisation from alcohol melted at 186° (decomp.). It was shown to be *p*-bromobenzeneseleninic acid (Found: Se, 29·0. Calc.: Se, 29·3%). Nothing further was isolated. Reduction of the seleninic acid with zinc and hydrochloric acid gave di-*p*-bromophenyl diselenide, m. p. 113°, not depressing the m. p. of the product obtained from *p*-bromophenyl selenocyanate and potassium hydroxide (Found: C, 31·0; H, 2·0; Se, 33·4. Calc. for $C_{12}H_8Br_2Se_2$: C, 30·7; H, 1·7; Se, 33·6%). The diselenide gives the seleninic acid on treatment with warm nitric acid (*d* 1·41). Taboury (*loc. cit.*) gives the m. p. of di-*p*-bromophenyl diselenide as 107°. It was, however, obtained from a very complex mixture and was probably slightly impure.

Preparation and Nitration of p-*Dithiocyanobenzene*.—(*a*) Preparative details are given on p. 1374. After treatment with charcoal and crystallisation from acetone–light petroleum, the dithiocyanate forms white needles, m. p. 106°, only slightly volatile with steam (Found: N, 14·8; S, 33·5. $C_8H_4N_2S_2$ requires N, 14·7; S, 33·3%). On treatment with 50% alcoholic potassium hydroxide, followed by acidification, the dimercaptan is obtained. This melts at about 95° and in air or on treatment with alcoholic ammonia gives a white, odourless, insoluble solid, decomp. about 330°, which is probably polymerised *p*-phenylene disulphide (Leuchart, *J. pr. Chem.*, 1890, **41**, 205).

(*b*) The dithiocyanate (5 g.) was treated with nitric acid (*d* 1·41; 7 c.c.) and sulphuric acid (7 c.c.) at 5°. Ice (20 g.), added after 2 hours, gave a precipitate (6 g.; m. p. 141°) which on crystallisation from alcohol formed yellow needles, m. p. 143—144° (Found: N, 17·7; S, 27·5. $C_8H_3O_2N_3S_2$ requires N, 17·7; S, 27·0%). The nitro-dithiocyanate did not depress the m. p. (143—144°) of the

product obtained from 4-chloro(or bromo)-3-nitroaniline or from 2-nitro-4-thiocyanoaniline (see pp. 1373, 1374) by the diazo-reaction.

Preparation and Nitration of p-*Thiocyanoselenocyanobenzene.*—Preparative details are given on p. 1374. The crude reaction product was dried, extracted with chloroform, decolorised with charcoal, and crystallised from chloroform–light petroleum or from alcohol, giving white needles, m. p. 109—110°, which were somewhat volatile with steam and very soluble in acetone and chloroform (*Found*: N, 11·7; S, 13·8; Se, 32·9. $C_8H_4N_2SSe$ *requires* N, 11·7; S, 13·4; Se, 33·05%).

p-Thiocyanoselenocyanobenzene (2 g.) was dissolved in nitric acid (*d* 1·41; 6 c.c.) and sulphuric acid (7 c.c.) at 3°. Treatment with ice after 1 hour gave white crystals (1·5 g.), m. p. 154° after recrystallisation from acetone and alcohol. These contained sulphur, selenium, and nitrogen, were completely soluble in cold sodium bicarbonate solution or in hot water, gave no colour with alcoholic alkali, and contained either an SCN or an SeCN group as shown by the production of potassium thiocyanate on their reacting with alcoholic potassium hydroxide (R·SCN+KSH=RSK+HSCN. R·SeCN+KSH=RSeK+HSCN). The SeCN group had apparently been oxidised as before, giving *p*-thiocyanobenzeneseleninic acid (Found: N, 5·8; Se, 32·0. $C_7H_5O_2NSSe$ requires N, 5·7; Se, 32·1%). The use of nitric acid (*d* 1·41) or of the 95% acid alone or mixed with acetic acid or acetic anhydride at temperatures from −20° to 60° gave either the unchanged substance or the seleninic acid.

Nitro-derivatives of p-*Thiocyanoaniline and of* p-*Thiocyanoacetanilide.*—*p*-Thiocyanoaniline (Kaufmann and Oehring, *Ber.*, 1926, **59**, 189) was warmed with acetic anhydride, giving the acetyl derivative, m. p. 187° (Fichter and Beck, *Ber.*, 1911, **44**, 3636, give 181°). This (7·2 g.) was nitrated in a mixture of nitric acid (*d* 1·41; 17 g.) and sulphuric acid (25 g.) at 3°. Addition of ice after 2 hours gave a solid (9 g.), which crystallised from alcohol in yellow needles of 2-*nitro*-4-*thiocyanoacetanilide*, m. p. 138—139° (Found: N, 18·0; S, 13·7. $C_9H_7O_3N_3S$ requires N, 17·7; S, 13·5%). The mother-liquors yielded a small quantity of orange crystals, m. p. 113°, not depressing the m. p. of 2-*nitro*-4-*thiocyanoaniline* obtained by gently warming the nitro-acetanilide with hydrochloric acid for 10 minutes on the steam-bath. Dilution with ice gave a product, m. p. 113°, which was crystallised from aqueous alcohol (Found: N, 21·6; S, 16·3. $C_7H_5O_2N_3S$ requires N, 21·5; S, 16·4%). The prolonged action of hydrochloric acid on this substance gives red needles, m. p. 189°, which are possibly di-3-nitro-4-aminophenyl disulphide, but they have been only superficially examined

(Found: N, 16·15. Calc. for $C_{12}H_{10}O_4N_4S_2$; N, 16·5%). They are also obtained from 2-nitro-4-thiocyanoaniline and alcoholic alkali; the substance separates from acetone as yellow needles, which lose acetone at 100°, giving the red compound, m. p. 169°.

The position of the nitro-group in 2-nitro-4-thiocyanoaniline was determined by diazotisation in alcoholic solution, which gave rise to *m*-nitrophenyl thiocyanate, m. p. and mixed m. p. 56°. The diazo-group was also replaced by chlorine, bromine, thiocyanogen and selenocyanogen, giving (*a*) *4-chloro-3-nitrophenyl thiocyanate*, m. p. 63°, not depressing the m. p. of the product obtained from 4-chloro-3-nitroaniline by the Sandmeyer reaction, (*b*) *4-bromo-3-nitrophenyl thiocyanate*, m. p. 83°, pale yellow needles from light petroleum (Found: N, 11·0. $C_7H_3O_2N_2BrS$ requires N, 10·8%), (*c*) nitro-*p*-dithiocyanobenzene, m. p. 143—144° (see pp. 1365, 1371, and below), and (*d*) *2-nitro-4-thiocyanophenyl selenocyanate*, m. p. 147°, yellow needles from alcohol, giving a purple colour with alcoholic alkali (Found: N, 14·9; Se, 27·3. $C_8H_3O_2N_3SSe$ requires N, 14·8; Se, 27·8%). In these preparations the nitrothiocyanoaniline was not isolated, the solution of its acetyl derivative in warm hydrochloric acid being diazotised (see table on p. 1374).

In the case of reactions summarised in this table further experimental details are omitted, the procedure closely resembling that employed in the preparation of such compounds as nitro-*o*-tolyl thiocyanate and phenyl selenocyanate (p. 1368); the yields are usually not less than 60—70%.

Abnormal Behaviour of 4-Chloro (and *bromo*)*-3-nitrobenzenediazonium Salts with Thiocyanates.*—4-Bromo-3-nitroaniline (22 g.) in dilute sulphuric acid (1 : 3) was diazotised at 3° with sodium nitrite (9 g.), and the solution slowly added in the cold to potassium thiocyanate (14·5 g.; 1·5 mols.) and cuprous thiocyanate (20 g.) in water. After 12 hours, the solid obtained was repeatedly extracted with alcohol. This finally yielded 9 g. of pale yellow needles (K), m. p. 143—144°, which were free from halogen, contained the thiocyano-group, and did not depress the m. p. of the product similarly obtained from 4-chloro-3-nitroaniline, or that of nitro-*p*-dithiocyanobenzene (p. 1371) obtained by nitration of *p*-dithiocyanobenzene or from 2-nitro-4-thiocyanoaniline (Found: N, 17·9; S, 27·5. Calc. for $C_8H_3O_2N_3S_2$: N, 17·7; S, 27·0%).

The alcoholic mother-liquors deposited a solid which, on repeated crystallisation from light petroleum, formed yellow needles (L; 10 g.), m. p. 83°, containing halogen and the thiocyano-group, and not depressing the m. p. of 4-bromo-3-nitrophenyl thiocyanate obtained from 2-nitro-4-thiocyanoaniline (above and p. 1374) (Found: N, 11·0. Calc. for $C_7H_3O_2N_2BrS$: N, 10·8%).

Base.	Wt. of base (g.).	H_2SO_4 (c.c.).	Acid : water.	Conc. HCl (c.c.).	$NaNO_2$ (g.).	KSCN (g.).	KSeCN (g.).	Cu' salt (g.).	Product.	M. p.	Coloration with alc. KOH.
$NH_2 : NO_2 : Cl = 1 : 3 : 4$	17	100	1 : 4	—	9·0	13·5	—	20·0	$SCN : NO_2 : Cl = 1 : 3 : 4$	63°	Red
									$SCN : NO_2 : SCN = 1 : 3 : 4$	144	,,
$NH_2 : NO_2 : SCN = 1 : 2 : 4$	1·5 in 10 c.c. alcohol	10	conc.	—	0·5	—	—	—	$H : NO_2 : SCN = 1 : 2 : 4$	56	,,
	3·0	—	—	10	0·9	—	—	2·5 in conc. HCl (30 c.c.)	$Cl : NO_2 : SCN = 1 : 2 : 4$	63	,,
	8·0	—	—	30	3·6	—	—	12·0 in HBr (50 c.c.; d 1·49)	$Br : NO_2 : SCN = 1 : 2 : 4$		,,
	3·0	—	—	10	2·0	1·7	—	4·0	$SCN : NO_2 : SCN = 1 : 2 : 4$	144	,,
	12·0	—	—	35	4·5	—	11·0	—	$SeCN : NO_2 : SCN = 1 : 2 : 4$	147	Purple
$NH_2 : SCN = 1 : 4$	7·8	30	1 : 4	—	3·6	6·2	—	10·0	$SCN : SCN = 1 : 4$	106	—
	20·0	120	1 : 4	—	12·0	—	30·8	—	$SeCN : SCN = 1$	100·5	—
$NH_2 : NO_2 = 1 : 3$	14·0	50	1 : 3	—	9·0	—	21·0	—	$SeCN : NO_2 = 1 : 3$	65	Red
$NH_2 : NO_2 : CH_3 = 1 : 3 : 4$ / $NH_2 : NO_2 : CH_3 = 1 : 2 : 4$	5·0	30	1 : 4	—	4·0	—	8·0	—	$SeCN : NO_2 : CH_3 = 1 : 3 : 4$	69·5	,,
									$SeCN : NO_2 : CH_3 = 1 : 2 : 4$	150	Purple
$NH_2 : NO_2 : Cl = 1 : 2 : 4$	5·0	25	1 : 3	—	2·5	—	7·0	—	$SeCN : NO_2 : Cl = 1 : 2 : 4$	127	,,
$NH_2 : NHAc = 1 : 4$	7·5	40	1 : 3	—	4·5	—	11·0	—	$SeCN : NHAc = 1 : 4$	205	—

Analogous treatment of 4-chloro-3-nitroaniline (17 g.) gave (K), 9 g., m. p. 143—144°, and pale yellow needles (M; 10 g.), m. p. 63°, containing halogen and the thiocyano-group, not depressing the m. p. of 4-chloro-3-nitrophenyl thiocyanate obtained from 2-nitro-4-thiocyanoaniline (Found: N, 13·3. Calc. for $C_7H_3O_2N_2ClS$: N, 13·1%). When ferric thiocyanate was employed instead of the copper salt (Korczyński, *Bull. Soc. chim.*, 1922, **31**, 1179), the same products were obtained (K, 12·5 g.; M, 8 g.).

Nitro-derivatives of p-*Selenocyanoaniline and* p-*Selenocyano-acetanilide.*—*p*-Selenocyanoaniline (J., 1926, 1654) was dissolved in warm acetic anhydride, giving the *acetyl* derivative as white crystals, m. p. 206° (Found: N, 11·9. $C_9H_8ON_2Se$ requires N, 11·7%). This did not depress the m. p. of the product obtained from diazotised *p*-aminoacetanilide and potassium selenocyanate (see p. 1374), the reaction mixture being left for 1 day.

The selenocyanoacetanilide (4 g.) was added to nitric acid (*d* 1·5; 10 c.c.) at −20°, and the solution poured on ice after 1 hour. Fractional crystallisation of the yellow product gave almost equal amounts of yellow needles (H), m. p. 157°, and an almost white solid (J), m. p. 215°. (H) was found to be 2-*nitro*-4-*selenocyanoacetanilide* (Found: N, 15·2. $C_9H_7O_3N_3Se$ requires N, 15·0%). (J) was almost completely soluble in sodium bicarbonate solution and appeared to be a slightly impure seleninic acid. It has not been further examined.

On warming with hydrochloric acid, (H) gave a clear solution, from which ice precipitated a solid, forming, on crystallisation from aqueous alcohol, orange needles, m. p. 118°, which were 2-*nitro*-4-*selenocyanoaniline* (Found: N, 17·3. $C_7H_5O_2N_3Se$ requires N, 17·3%).

The selenium determinations were carried out by heating the substance with fuming nitric acid for 60 hours at 300°, evaporating the mixture with hydrochloric acid, and precipitating the selenium with sulphur dioxide. This method gives somewhat low results owing to volatilisation of selenium (Lyons and Shinn, *J. Amer. Chem. Soc.*, 1902, **24**, 1085; Bradt and Lyons, *ibid.*, 1926, **48**, 2642), but the error is not serious.

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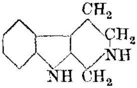
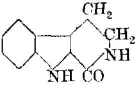
THE UNIVERSITY, MANCHESTER. [*Received, March* 10*th*, 1928.]

NOTES.

3 : 4 : 5 : 6-*Tetrahydro-4-carboline.* By JULIUS NICHOLSON ASHLEY and ROBERT ROBINSON.

3 : 4 : 5 : 6-TETRAHYDRO-4-CARBOLINE (tetrahydronorharman) (I) has been obtained by Asahina, Irie, and Ohta (*J. Pharm. Soc. Japan*, 1927, No. 545) by the reduction of a degradation product of evodiamine. The substance can also be readily prepared by the reduction of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (II) by means of sodium and *n*-butyl alcohol.

(I.) 

 (II.)

Experimental.—β-3-Indolylpropionhydrazide, m. p. 140—141°, and 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline, m. p. 185—186°, were readily obtained in satisfactory yield by the methods of Manske and Robinson (J., 1927, 240), but the melting points formerly ascribed to these substances are about 10° too low, evidently as the result of an unsuspected gross error in the thermometer, since the original specimens have been re-examined and found to melt at 140—141° and 185—186°, respectively.

Sodium (10 g.) was gradually added to a boiling solution of 3-keto-3 : 4 : 5 : 6-tetrahydro-4-carboline (4 g.) in *n*-butyl alcohol (100 c.c.). After 2 hours' refluxing, 90% alcohol (100 c.c.) and water (100 c.c.) were successively introduced and the mixture was distilled in a current of steam. The pale brown residue in the flask crystallised from alcohol (charcoal) in colourless, elongated prisms, m. p. 204° (Found: C, 76·6; H, 7·0; N, 16·5. Calc. for $C_{11}H_{12}N_2$: C, 76·7; H, 7·0; N, 16·3%). The salts of the base are readily soluble in water and the nitroso- and acetyl-derivatives are insoluble in dilute hydrochloric acid. The picrate crystallises from acetone-alcohol in bright canary-yellow, prismatic needles, m. p. 249—251° (decomp.). Asahina, Irie, and Ohta (*loc. cit.*) state that their base, $C_{11}H_{12}N_2$, has m. p. 204—205° (picrate, m. p. 250—251°).

On oxidation of the base with chromic acid in hot dilute sulphuric acid, norharman was obtained in poor yield; after purification, this had m. p. 198°, not depressed on admixture with an authentic specimen.—THE UNIVERSITY, MANCHESTER. [*Received, April 11th*, 1928.]

The Occurrence of Titanium Tetrachloride in Commercial Disilicon Hexachloride. By FREDERIC STANLEY KIPPING and REGINALD AUBREY THOMPSON.

IN the course of some experiments with disilicon hexachloride, which was kindly supplied by Messrs. Albright and Wilson, it was observed that the addition of 0·3—0·5 c.c. of the hexachloride to purified ether (100 c.c.) caused the development of a yellow colour; this occurred not only with the crude material, but also—although in a less marked manner—with samples which had been fractionated twice through a 12-inch rod and disc column, boiled at 145—147°, and contained Cl 78·7% (Si_2Cl_6 requires 78·9%). When, on the other hand, about 1 c.c. of ether was added to the fractionated hexachloride (100 c.c.) there was an immediate precipitation of a small proportion of a yellow, crystalline substance. This product melted at 42—45° and was doubtless identical with the compound $TiCl_4,(C_2H_5)_2O$ which Bedson obtained by the direct combination of titanium tetrachloride and ether (J., 1876, **29**, 311). The presence of titanium tetrachloride in the disilicon hexachloride was also proved by the hydrogen peroxide reaction, and with thymol and sulphuric acid; by reduction and titration with iron alum its quantity in the twice fractionated sample was found to be 1·6%. For the complete separation of the titanium tetrachloride (b. p. 135°) from the disilicon hexachloride (b. p. 147°) repeated fractionation through a rod and disc column is necessary; after five or six operations the hexachloride gives no colour reaction with hydrogen peroxide solution.

The compound $TiCl_4,(C_2H_5)_2O$ (b. p. 118—120°) cannot be easily separated from the disilicon hexachloride by distillation; when it is decomposed by alkali and the aqueous solution is then distilled, the distillate gives a distinct iodoform reaction.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, March 24th*, 1928.]

Fission of the Pyridine Nucleus by Oxidation with Alkaline Potassium Permanganate. By BRIAN DUNCAN SHAW and ARTHUR LESLIE WILKIE.

THE fact that the pyridine nucleus can be ruptured by the action of either acid or alkaline permanganate was observed by one of us (B. D. S.) in 1921. The results with the former reagent agreed entirely with the observations of Delépine (*Compt. rend.*, 1927, **184**, 206). A more extended investigation of the action of alkaline permanganate was commenced, but as one of us has been obliged to abandon the work, the initial results are now given.

Pure pyridine (5 g.) was boiled with water (250 c.c.), and finely powdered potassium permanganate added in quantities of 5 g. at a time until a permanent pink colour resulted (50 g. during 12 hours). The odour of pyridine had then vanished. A deposit of ammonium carbonate appeared in the condenser during the first hour. The manganese dioxide was removed, and the filtrate evaporated to dryness. The white, deliquescent residue was a mixture of the potassium salts of carbonic, oxalic, nitric and nitrous acids. The quantity of potassium permanganate used was only about two-thirds of that calculated from the equation $2C_5H_5N + 11O_2 = 10CO_2 + 2NH_3 + 2H_2O$.

The fact that the nucleus itself is attacked by alkaline permanganate accounts for the low yields of pyridinecarboxylic acids, obtained by the oxidation of side chains with this reagent, when the solution is overheated.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, March 31st,* 1928.]

The Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. By ERWIN OTT.

Two communications bearing the title of this note (Lunt and Venkataswaran, J., 1925, **127**, 2052; 1927, 857) make it necessary to point out that experiments treating the same subject have been published by me (*Ber.*, 1925, **58**, 772). My results, however, are not in harmony with those of the two authors, who give for the decomposition of the carbon monoxide the equation $7CO = C_5O_3 + 2CO_2$, and for the brown solid the formula C_5O_3,xH_2O. By quantitative investigations of a different kind, and by definite evidence of the production of unimolecular C_3O_2 in the gases leaving the Siemens ozoniser, I showed that the equation of the decomposition is $4CO = C_3O_2 + CO_2$, and that the brown solid is the product of polymerisation of gaseous C_3O_2.—THE UNIVERSITY, MÜNSTER (WESTFALIA), GERMANY. [*Received, April 2nd,* 1928.]

Separation of Phthalic and Homophthalic Acids. By HARRY GORDON POOLE.

FOR the recovery of homophthalic acid from residues containing much phthalic acid, crystallisation is an unsatisfactory method. Practically complete separation is achieved, however, by means of the great difference in solubility of copper phthalate (Hermann, *Annalen*, 1869, **151**, 78), which is soluble in about 30 parts of water at 30°, and *copper homophthalate*, the solubility of which in water is less than 0·02% (1 part in 5000) at 25° and less than 0·01% at 100°.

The homophthalate is precipitated from mixed solutions of copper sulphate and sodium homophthalate in greenish-blue, microscopic crystals which, owing to their insolubility in ordinary neutral organic solvents, are difficult to obtain in a perfectly pure condition (Found : Cu, 25·3. $C_9H_6O_4Cu$ requires Cu, 26·2%). They readily become electrified when rubbed with a glass rod.

In order to separate homophthalic acid from phthalic acid, the mixture is neutralised with sodium hydroxide and diluted considerably, and a solution of copper sulphate is added in the cold. (If a solution of copper phthalate containing copper sulphate is boiled, a greenish-blue, flocculent precipitate, apparently of a basic salt, is formed.) After 12 hours the flocculent precipitate is filtered off, washed, and treated with concentrated hydrochloric acid and sufficient water to dissolve the mass on boiling. The homophthalic acid separates on cooling, in good crystals having the correct melting point, 181°. From an artificial mixture of phthalic acid (66·6%) and homophthalic acid (33·3%), 90% of the homophthalic acid was recovered in this way.—UNIVERSITY OF MELBOURNE. [*Received, April 11th*, 1928.]

Arrhenius Memorial Lecture.

DELIVERED ON MAY 10TH, 1928.

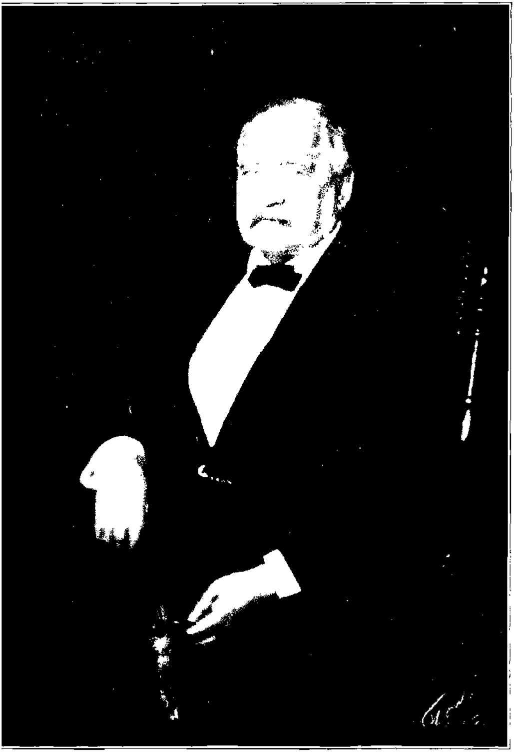
By SIR JAMES WALKER, F.R.S.

A LITTLE over forty years ago the conjunction of the ideas of osmotic pressure and of electrolytic dissociation ushered in a new era in the development of the physical chemistry of solutions—an era of unexampled fertility. Van 't Hoff and Arrhenius, the originators of these new ideas, have now both passed away. It is sixteen years since I was charged by the Society to deliver the van 't Hoff memorial lecture. To-day it is my task to discharge a similar duty in honour of Arrhenius. My relations to these men were altogether different; Arrhenius was a close friend, van 't Hoff a remote immortal. The sketch of the life and work of Arrhenius which I present is therefore not that of a completely detached historian, but is shaped by personal reminiscence and tinged with personal affection.*

I well remember when I first encountered his name. It was in the autumn of 1887 in the small departmental library of Baeyer's laboratory in Munich. On a shelf there lay the loose numbers of the first volume of the *Zeitschrift für physikalische Chemie*, newly founded by Ostwald. Turning over the pages of this interesting new journal, I saw what seemed to me the very odd name of Svante Arrhenius as author of a paper on the influence of neutral salts on the velocity of saponification of ethyl acetate. I did not find this paper of more than moderate interest, but later in the year there was published another by the same author on the dissociation of substances dissolved in water. This was plainly a novel and striking conception, and although I was not altogether convinced by the arguments it contained, I marked it for closer study at a later time.

In the spring of the following year I left Munich for Leipzig and was caught in the wave of Ostwald's enthusiasm for the new doctrines of osmotic pressure and electrolytic dissociation. In Ostwald's laboratory I used to work in a small room with Wilhelm Meyerhoffer, who afterwards collaborated with van 't Hoff in his phase-rule investigations. One day Meyerhoffer burst into the room, and pointing excitedly along the corridor, said: "Arrhenius is

* I take this opportunity of thanking the many friends both Swedish and English to whom I am indebted for information regarding Arrhenius. A bibliography of his work up to 1908 is to be found in *Z. physikal. Chem.*, vol. **69**, and up to 1918 in ***Medd. K. Vetenskapsakad.*** *Nobel-institut*, vol. **5**.



SVANTE AUGUST ARRHENIUS.

[To face p. 1380.]

there." I peered out and saw a stoutish fair young man talking to Ostwald near the entrance hall. It was Arrhenius. We were made acquainted by Ostwald, but at that time I saw little more of him. Next year he came to work in Leipzig, and I had the opportunity of meeting him daily. He was one of the simplest and least assuming of men. He gave himself no airs and treated us young fellows as if we were his scientific equals, although at that time he was being recognised in Germany as a leading spirit in physical chemistry. In his own country he was still unregarded.

Svante Arrhenius came of Swedish farmer folk, a remote ancestor being one Lasse Olofsson, who in 1620 moved to the village of Årena, from which the family derived its surname in the Latinised form of Arenius, the spelling being changed in the early part of the nineteenth century to Arrhenius by the uncle of Svante, Professor Johan Arrhenius, a botanist and secretary of the Academy of Agriculture. Johan and his younger brother, Svante Gustav Arrhenius (1813—1888), the father of our Svante, went as students to the University of Upsala, and the latter subsequently established himself in that town as a land surveyor. He was appointed collector to the University, but the emoluments of the post were so meagre that he was forced to undertake in addition the management of the estate of Wijk, on Lake Mälar, which belonged to Count von Essen. He married in 1855 Caroline Thunberg, and at Wijk there was born on 19 February, 1859, a son whom they called Svante August Arrhenius. Owing to improved prospects the family moved to Upsala in the beginning of 1860. Young Svante was educated at the Cathedral School of Upsala, and was fortunate in the fact that the Rector of the school was a good teacher of physics. He left at the age of seventeen with a good record in mathematics and physics to enter the University of Upsala, where he soon passed the candidate's examination, admitting to study for the doctorate. It seems to have been his original intention to take chemistry as his main subject under Cleve, well known for his investigations on the rare earths and on complex ammoniacal compounds. Cleve, however, was apparently an uninspiring teacher and neglected the theoretical side of chemistry. Arrhenius records that he never heard any mention from the rostrum of the periodic law, although it was already ten years old, nor when he came to write his thesis had he any knowledge of the existence of the law of Guldberg and Waage, which was even older. In 1881 he definitely turned to physics, although the conditions for its study in Upsala were far from ideal. Thalén was at that time Professor of Physics there. His reverence for his master and predecessor Ångström was so great that, beyond the apparatus

for elementary students, there was little else in the department but instruments for exact measurements of wave-lengths, a subject for which Arrhenius had no liking. Thalén did not encourage independent work in his laboratory, and Arrhenius was forced to look about for some other opportunity to begin physical research. He, with a fellow student, repaired in September 1881 to Stockholm with the intention of working in the laboratory of Erik Edlund, Professor of Physics to the Swedish Academy. Edlund gave them a hearty welcome, and they began by assisting him in his work on electromotive forces in the spark discharge. In the spring of the following year Arrhenius started his first independent research on the decay of galvanic polarisation with time, an account of which was published in the *Bihang* of the Swedish Academy in 1883. From this he passed to the measurement of the conducting power of electrolytic solutions.

It is of interest to enquire into the reasons which induced Arrhenius to take up this line of work. The pursuit of science, like other human activities, is not exempt from the prevalence of fashions. At the period under consideration the study of the properties of solutions was in the air. Van 't Hoff was busy tracing the analogy between dilute solutions and gases, Raoult was developing empirical methods for the determination of the molecular weights of dissolved substances, Kohlrausch had just perfected his telephone method for determining electrolytic conductivities, Ostwald was working at reaction velocities and the affinities of acids and bases in aqueous solution. Arrhenins yielded to the same influenee, but curiously enough what led him to the investigation of electrolytic solutions was not directly concerned with the conducting substances themselves. He tells us that Cleve in his lectures had emphasised the impossibility of ascertaining the molecular weights of substances, such as sugar, which could not be volatilised without decomposition. Arrhenius rightly recognised that this was a great drawback, by the removal of which a considerable advance in chemistry would be rendered possible. He was unaware of Raoult's work, and thought that some light might be thrown on the molecular weight of dissolved substances by measurements of electrolytic conductivity. He knew that when some of the water of a conducting solution was replaced by more complex non-conducting substances, such as alcohol, the conductivity was lowered, and he thought it might be feasible to deduce the molecular weight of this added substance from its effect on the conductivity. He had not proceeded far with his measurements, however, when he recognised that the state of the conducting salt was the matter of primary importance.

The theory of electrolysis and electrolytic solutions was also decidedly in the air at the same period. The chains of Grotthus, the hypothesis of Clausius on continual momentary separation of ions, Hittorf's work on migration, Helmholtz's conception of the atomic nature of electricity, the work of Kohlrausch on conductivity, were all leading up to some definite comprehensive theory which in the end was furnished by Arrhenius.

Arrhenius completed his experimental work in the spring of 1883 and wrote the theoretical part at his home in the summer of the same year. The memoir containing the results of his conductivity experiments and the conclusions he deduced from them was submitted to the Swedish Academy of Sciences in June 1883, and published in the following year (*Bihang*, vol. **8**, Nos. 13 and 14). It is in French and is entitled "Investigations on the galvanic conductivity of electrolytes. Part I. Determination of the conductivity of extremely dilute solutions by means of the depolariser. Part II. Chemical theory of electrolytes." Arrhenius undertook the experimental investigation of dilute solutions himself, for although Kohlrausch had made similar measurements and had quoted some numerical data, the final publication of his results was delayed till 1885. The depolariser which Arrhenius used was an apparatus devised by Edlund in 1875, and corresponds roughly to a hand-driven rotating commutator. It is of interest to note that the conductivity cell which bears Arrhenius's name is described in this paper.

Arrhenius measured the resistance of a considerable number of salts, acids and bases at various dilutions, sometimes as high as $v = 10{,}000$. Unfortunately the actual dilutions are not given, so that it is difficult to correlate the data of Arrhenius with those of other authors. He tabulated his results so as to show in what ratio the resistance of an electrolyte is increased when the dilution is doubled. This ratio, as Kohlrausch had found earlier, is nearly equal to 2 for most salts, *i.e.*, specific conductivity is nearly proportional to concentration. Departure from this ideal value he took as a basis for classification of the dissolved electrolytes, and showed that chemically similar substances fell into the same category when classified according to dilution-ratios. A discussion of the data led Arrhenius to the conclusion that "if on dilution of a solution the conductivity does not change proportionally to the amount of electrolyte, then a chemical change has occurred on addition of the solvent." He exemplifies this by the consideration of potassium cyanide with the abnormally high dilution ratio of 2·14, which he attributes to the partial splitting of the salt into acid and base on dilution with water. The abnormal values

obtained for soluble hydroxides and dilute solutions of acids he attributes to the presence of small quantities of ammonium carbonate in the solvent water.

The importance of this paper, however, does not lie in the experimental measurements or in the detailed deductions, but in the general ideas which Arrhenius developed in the second part. Instigated and encouraged by Otto Pettersson, then Professor of Chemistry in Stockholm, Arrhenius greatly expanded this theoretical section, which contains the germ of the later theory of electrolytic dissociation. He bases his theoretical treatment on the hypothesis of Williamson and Clausius. How this hypothesis presented itself to a clear and critical contemporary mind, unacquainted with the work of Arrhenius, may best be gathered from the admirable report on electrolysis presented by Oliver Lodge to the British Association in 1885.

Lodge writes: "No polarisation exists inside a homogeneous electrolyte; *there is no chemical cling of the atoms there, but only a frictional rub.* Such a fact as this, if well established, renders necessary *some form* of dissociation hypothesis. The form of dissociation hypothesis suggested by Clausius and Williamson is well known. It supposes that the vast majority of molecules in an electrolyte are quite insusceptible to the influence of electrodes, but that a few of them (the number being increased by complexity of composition and rise of temperature) are, by collision or otherwise, dissociated and exist in the free atomic state, each atom with its appropriate charge. These alone feel the influence of the electrodes. . . . Individual atoms, although permitted to combine as soon as they like, on this theory, are commonly thought of as existing in the dissociated state for a finite time. If there are chemical or other objections to such a view, it need not be held; all that the facts of electrolysis require is the most momentary dissolution of partnership—temporary but quite perfect freedom. . . . Provided a sufficient supply of snch temporary severances occurs throughout the liquid, no individual atom need remain uncombined for a thousandth of a second, so far as the phenomena of electrolysis are concerned."

Arrhenius derives from the hypothesis the notion of closed circular currents in the electrolytic solntion in its normal state (*i.e.*, when not undergoing electrolysis) which are due to the separation of the ions and their recombination with other than their original partners. This notion he uses in dealing with the equilibrium between electrolytes in aqueous solutions. But by far the most important original idea, on which he bases his further treatment, is that of the distinction of the dissolved molecules into

active and inactive. He arrives at it in the following way. A solution of ammonia exhibits a feeble molecular conductivity which increases with dilution. This Arrhenius attributes to the progressive conversion of the non-electrolytic NH_3 into the electrolytic NH_4OH as dilution is increased. He proceeds: "It has been shown that pure anhydrous hydrochloric acid is a non-conductor, that is, a non-electrolyte. If water is added to it, it is converted into an electrolyte, naturally in a progressive manner. It is impossible to deny the complete analogy of this phenomenon with that occurring on the dilution of ammonia or acetic acid, although it takes place much more rapidly." He sums up in the following statement: "The aqueous solution of any hydrate [*i.e.*, acid or base] is composed, in addition to the water, of two parts, one active (electrolytic), the other inactive (non-electrolytic). These three substances (*viz.*, water, active hydrate, and inactive hydrate) are in chemical equilibrium, so that on dilution the active part increases and the inactive part diminishes."

Arrhenius gives nowhere in this memoir a precise account of the nature of the active and inactive portions. He indicates and illustrates what they might be, but that is all; he does not define. The most important special feature of the paragraph is the statement that the active part increases on dilution. He continues: "In what respect these two parts differ remains to be elucidated. Probably the active part (as with ammonia) is a compound of the inactive part and the solvent. Or possibly inactivity may be caused by the formation of molecular complexes. Or again the difference between the active and inactive parts may be purely physical. The same statement applies to bases, and we may also speak of the inactivity of dissolved salts, in which case the notions of inactivity and complexity completely coincide."

With regard to solutions of normal salts he makes the following statements: (1) "Aqueous solutions of all electrolytes contain the dissolved electrolyte at least in part in the form of molecular complexes. (2) If the attenuation of the solution of a normal salt is continued, *the complexity approaches asymptotically an inferior* limit. (3) The limit to which the complexity of a normal salt at extreme dilution tends to approach is of the same degree for all normal salts. Probably this limit will not be attained before all the salts are split up into simple molecules, represented by the chemical molecular formula."

"To fix our ideas, I have introduced the notion of coefficient of activity defined as follows:—The coefficient of activity of an electrolyte is the number expressing the ratio of the number of ions actually contained in the electrolyte to the number of ions it

would contain if the electrolyte were completely transformed into simple electrolytic molecules."

" Before going on we shall describe more precisely the notion of coefficient of activity by the aid of the hypothesis of Williamson and Clausius. According to § 2 this coefficient is defined by the number of ions present in a solution. But to each pair of ions there corresponds an electrolytic molecule which can take part in the production of a circular current; that is to say, its ions are endowed with the movement assumed by the hypothesis. If now *an electrolyte is constituted in such a manner that only a certain* fraction $1/n$ can at the same time take part in such a movement, it is evident that its coefficient of activity is $1/n$. It is not necessary, however, that a chemical difference should exist between the active and inactive parts. For greater clearness we choose an ammoniacal solution as example. In this solution there are two different parts, one active NH_4OH, the other inactive NH_3. If the latter is transformed into the former, the sum of the molecules of the two species is not augmented. Thus if m and n are the numbers of molecules of NH_4OH and NH_3, the first factor of the coefficient of activity will be $\frac{m}{m+n}$. Now several of the NH_4OH molecules may be associated with each other, so that the number of physical molecules of NH_4OH is p, of $(NH_4OH)_2$ q, of $(NH_4OH)_3$ r, etc., where evidently $p + 2q + 3r + \ldots = m$. Again of the molecules NH_4OH only a fraction $1/\lambda$ presents a simultaneous movement of ions. The corresponding numbers for $(NH_4OH)_2$ and $(NH_4OH)_3$ are $1/\mu$ and $1/\nu$. In this case the coefficient of activity of the ammonia will be equal to

$$\frac{m}{m+n}\left(\frac{p}{m\lambda}+\frac{q}{m\mu}+\frac{r}{m\nu}+\ldots\right)=\frac{1}{m+n}\left(\frac{p}{\lambda}+\frac{q}{\mu}+\frac{r}{\nu}+\ldots\right)."$$

It is interesting to compare with this coefficient of activity the " dissociation ratio " of Lodge, which is defined in the report from which I have already quoted. Lodge writes : " mn^3 is the number of grammes of the electrolysed or dissociated substance in a unit cube, and this we may write $N\mu$ where N stands for the number of monad gramme-equivalents of the really electrolysed substance per c.c. and μ is its molecular weight compared with hydrogen." Considering the case of two electrolytes dissolved in the same solution, he proceeds : " there will be N_1 and N_2 to represent the *amount of dissociated substance present, reckoned in gramme-*equivalents per cubic centimetre of solution. We come to the conclusion that we do not know the absolute velocity of any ion, and cannot know it without further information regarding the

dissociation ratio (that is N_1/N' or N_2/N') of each substance present, where N' is the total number of monad gramme-equivalents *of the dissolved substance* in a cubic centimetre of solution."

To Lodge the "dissociation ratio" is in all probability small. Arrhenius, on the other hand, contemplates the variability of the "coefficient of activity" with dilution and the likelihood of its being large in very dilute solutions.

So far the considerations are purely theoretical; now comes an important step, their union with experimental data. Kohlrausch had shown that the molecular conductivity of an electrolyte was additively composed of two terms, one depending on the positive radical and the other on the negative radical. But in extremely dilute solutions of salts the value for negative radicals was nearly the same; therefore, according to Arrhenius, "the molecular conductivity of the active part of an acid (in dilute solution) is constant and independent of the nature of the acid," and as a corollary from this "the better the (dilute) solution of an acid conducts electricity, the greater is its active part." For want of precise data for calculating the absolute value of the coefficient of activity, Arrhenius takes it as proportional to the molecular conductivity. Thus he is enabled to compare the activities of acids amongst themselves, and of bases amongst themselves. He finds at once that the activities of acids as thus determined from their conductivities agree well with our general notions regarding their strengths, and is led to the statement that "for acids and bases galvanic activity is accompanied by chemical activity." He proceeds to discuss double decomposition in electrolytic solutions, on somewhat hypothetical grounds, and arrives at a formula (containing coefficients of activity) which he applies practically to many important reactions. If in the general equation of double decomposition

$$\begin{array}{ccccccc} AB & + & CD & \rightleftharpoons & AD & + & BC, \\ 1-x & & n-x & & p+x & & q+x \end{array}$$

are the molecular proportions at equilibrium, and

$$\alpha \qquad \delta \qquad \beta \qquad \gamma$$ are the coefficients

of activity of the various substances, then at equilibrium

$$(1-x)(n-x)\alpha\delta = (p+x)(q+x)\beta\gamma.$$

If the action considered is

$$\text{Acid} + \text{Base} \rightleftharpoons \text{Salt} + \text{Water}$$

the product of the coefficients of activity on the left is, when acid and base are strong, enormously greater than the product of those on the right, and salt-formation is, therefore, practically complete.

If acid or base is weak, the two products are comparable, and in consequence, entire neutralisation will not take place, notable quantities of acid and base remaining free. If the activity coefficient of one of the substances (say alcohol regarded as acid) is smaller than that of water, only traces of the salt are formed. Here we find a definite treatment of salt-hydrolysis based on the following principle: "What is common to all these cases is the necessity of regarding water as an acid (or as a base) which competes with other acids (or bases) present in the equilibrium." Arrhenius states further the proposition, which requires some restriction, that "at a dilution not excessively great the quantity of salt decomposed is approximately proportional to the square root of the quantity of the solvent water."

The theory is then applied to the displacement of one acid by another, to the influence of acid salts, and to equilibrium in heterogeneous systems. The consequences of the variation of the coefficient of activity in homogeneous and in heterogeneous systems are considered, and sections are devoted to the behaviour of molten electrolytes and to thermochemistry. He deduces the following important principle: "The heat of neutralisation evolved by the transformation of a base and an acid, both perfectly active, into water and a simple salt, is nothing but the heat of activation of water."

After a review of anterior theories Arrhenius summarises his work thus: "We have first shown the probability that electrolytes can assume two different forms, one active, the other inactive, such that the active part is always, in the same external circumstances (temperature and dilution), a certain fraction of the total quantity of the electrolyte. The active part conducts electricity, and is thus in reality electrolytic; not so the inactive part. Moreover we have proved that the necessary consequence of the hypothesis of Clausius and Williamson is that there exist continuous circular currents, in which the active parts alone participate. The molecules participating in such currents are necessarily decomposed according to the scheme of double decomposition, new electrolytes being thereby formed. On this basis we have founded a chemical theory of electrolytes, which, being deduced from very probable sources, possesses also a high degree of probability. This theory leads to formulæ valid for chemical processes, formulæ very conformable to those proposed by Guldberg and Waage, which have been verified in a great number of instances. . . . As a provisional approximation we have assumed the coefficient of activity to be equal to the molecular conductivity. The numbers calculated on this hypothesis and the reactions thus foreseen, agree very well

with experimental facts. . . . These propositions and these laws are taken from the most different parts of chemical science; but as the theory agrees so well with reality on these different points, *it seems probable that it ought to do so also in intermediate regions.* . . . The theory is completely free from any hypothesis of an affinity different from physical forces, and in this respect is preferable to all prior theories. . . . True, it may be objected that the theory is only valid for electrolytes, while previous theories have embraced all substances. Against this we remark that chemical knowledge is mainly based on the reaction of electrolytes. . . . Reactions in general seem to manifest a considerable analogy to those of electrolytes, so that one could perhaps in the future enlarge the theory until it becomes, with some modification, applicable to all substances."

Nowhere does Arrhenius mention the word dissociation, although, as we have seen, the word is currently used by Lodge. The idea is, of course, there, but there is no identification of the "active part" of the electrolyte with free ions acting as separate molecules. The theory of electrolytic dissociation is as it were in solution in this memoir; it has yet to be crystallised out.

This comprehensive paper, which runs to 150 printed pages, was presented to the University of Upsala as a dissertation for the doctorate of the University. Its somewhat strange form is no doubt due to the use thus made of it. At the ends of sections and paragraphs there are numbered and italicised propositions, of widely different degrees of probability, and deduced by arguments of very different degrees of cogency. The paper then on a cursory inspection might convey an unfavourable impression if only the italicised portions were attended to. These propositions were probably the theses which were to be defended by the candidate in public debate with an opponent appointed by the University. The disputation passed off successfully and it must have been a bitter disappointment to Arrhenius when his dissertation was awarded a fourth class (*non sine laude approbatur*) and his defence a third (*cum laude approbatur*). After every allowance has been made for the novel and unusual character of the dissertation, it is difficult to see how the University of Upsala, the University of Bergman and Berzelius, should have condemned a brilliant thesis on the very subjects of affinity and electrochemistry associated with these names. For the award amounted to a condemnation; in view of it Arrhenius could not normally become a docent in the University of Upsala.

Arrhenius sent copies of his paper to Clausius, Lothar Meyer, Ostwald and van 't Hoff. "These celebrated men," he says, "with whom the Upsala professors were not to be compared,

treated me as a colleague and not as a stupid schoolboy." Ostwald was eminently friendly. He himself in his work on chemical dynamics was being drawn to the conclusion that velocities of reactions in which acids participate are connected with the electric conductivities of the acids. He writes (*J. pr. Chem.*, 1884, **30**, 93) "To test the idea I have during the past six months made preliminary experiments, which however have often been interrupted by other work. Meanwhile Svante Arrhenius, working in another range of ideas, undertook similar experiments and has published them in two memoirs, which also contain a very notable theory of chemical affinity developed from them. To the author of these memoirs, which belong to the most important ever published on the subject of affinity, there must be accorded not only priority of publication but priority of the idea."

Oliver Lodge was impressed by the paper and wrote for the Reports of the British Association in 1886 an abstract and critical analysis of it extending to 30 closely printed pages. "The paper seems to me a distinct step towards a mathematical theory of chemistry. The title affixed to it is 'The Chemical Theory of Electrolytes,' but it is a bigger thing than this: it really is an attempt at *an electrolytic theory of chemistry.*"

In August, 1884, Ostwald visited Arrhenius in Upsala, and his visit had a marked effect on Arrhenius's future. Ostwald undertook to get Arrhenius appointed as a docent in Riga, and the offer no doubt led to the favourable reception of an application by Arrhenius for a similar post in physical chemistry at Upsala. The two men had, while together, projected a scheme of research on physical chemistry to be undertaken in Ostwald's laboratory in Riga, but the illness and subsequent death of Arrhenius's father kept him in Upsala. Through Edlund's influence he received in December, 1885, a valuable travelling scholarship from the Academy of Sciences which enabled him to work in continental laboratories at discretion. The next five years were *Wanderjahre.* In 1886 he was with Ostwald in Riga, and Kohlrausch in Würzburg, during 1887 with Boltzmann in Graz, during 1888 with van 't Hoff in Amsterdam and again with Ostwald, now in Leipzig. In 1889 and 1890 he worked in the laboratories of Ostwald and Boltzmann. When in Sweden he lectured on physical chemistry in Upsala or worked in Edlund's laboratory in Stockholm. It was during this journeyman's period of his life that the theory of electrolytic dissociation was finally developed.

His original papers left the nature of the difference between the active and the inactive portions of the electrolyte unsettled, and the absolute value of the dissociation vague. As I have said, the

theory was still in solution. The nucleus which determined its crystallisation came through van 't Hoff's theoretical work on *osmotic pressure and his interpretation of Raoult's experimental* results.

Van 't Hoff, in a memoir presented to the Swedish Academy on 14 October, 1885, showed that it was possible to write for solutions an equation $PV = R'T$, analogous to the gas equation, where P, however, is the osmotic pressure instead of the gaseous pressure. The constant R' was in many cases equal to the gas-constant, but in many others differed from it. Van 't Hoff then wrote the general equation for dissolved substances in the form $PV = iRT$, where R is the gas-constant and i a coefficient sometimes equal to unity, but sometimes assuming values much greater, in particular for aqueous salt-solutions when the results are calculated from Raoult's experiments. For example, i is 1·98 for hydrochloric acid, 1·82 for sodium nitrate, and 1·78 for potassium chlorate. Van 't Hoff contented himself with these empirical values and made no attempt at an explanation. His paper was published in 1886, but Arrhenius did not receive a copy until March, 1887. On the 30th of that month he wrote to van 't Hoff from Würzburg: "Your paper has cleared up for me to a remarkable degree the constitution of solutions. If, for example, sodium chloride were normal in its behaviour, *i.e.*, if it consisted of simple molecules, its coefficient i would be equal to unity. But since i is much greater than unity, the natural explanation is to say that NaCl is partially dissociated, just as we say that at high temperatures I_2 is dissociated. Now this assumption might be deemed very rash, were it not that on other grounds we are led to look upon electrolytes as partially dissociated, for we assume that they decompose into their ions. But as these ions are charged with very great quantities of electricity of opposite sign, conditions are such that we cannot in all cases treat a solution of NaCl as if it simply consisted of Na and Cl. The pressure on the walls cannot, however, be appreciably affected, so that in this case the solution acts as if Na and Cl were free. And when we consider which substances (according to Raoult's experiments) are abnormal, it is not the inorganic (*e.g.*, not $HgCl_2$, CO_2, H_2S, etc.), but the electrolytic substances (*i.e.*, substances which are conductors of the same order as salts) even when they are organic, *e.g.*, oxalic acid. Trichloroacetic acid and sulphonic acids must show this still more clearly when they come to be investigated. Since according to the above assumption electrolytes decompose into their ions, the coefficient i must lie between unity and the number of the ions. This in reality holds good: for example, the coefficient nearly reaches 2 for NaCl, KCl, KNO_3, NaOH, etc., which have two ions;

for $Ba(OH)_2$, $CaCl_2$, K_2SO_4, etc., which have three ions, it almost approaches 3, and so on. . . . From the above assumption we can even calculate the value of i from the conductivity, and this I shall probably soon carry out; till now time has failed me. What I called in my paper 'Sur la conductibilité' active molecules, are thus the same as dissociated molecules. One of the propositions which I then put forward would now be written :—In all probability all electrolytes are completely dissociated at the most extreme dilution." Here we have the first appearance of the theory of electrolytic dissociation. If we cannot fix its birthday, at least we can its birth-month. It is clear, definite, and concise, and all Arrhenius's previous theoretical treatment can easily be translated into terms of it. Van 't Hoff accorded the new idea a favourable reception. He replied on April 7 : "Your statement that the number of ions roughly keeps pace with the values of i, and that the conductivity also increases with i, agrees with most of the cases known to me." . . . He remarks that he had always thought of the dissociation into ions as being confined to an extremely small portion of the salt, but confesses that he sees no grave difficulty in assuming a greater dissociation. Arrhenius in a letter dated 13 April is pleased to learn that this is van 't Hoff's view, and states that Emil Fischer, with whom he had discussed the matter in Würzburg, although he was friendly to the idea, was of opinion that most chemists would be opposed to such far-reaching dissociation. Arrhenius continues : "It is true that Clausius had only assumed that a minute quantity of a dissolved electrolyte is dissociated, and that all other physicists and chemists had followed him; but the only reason for this assumption, as far as I can understand, is a strong feeling of aversion to a dissociation at so low a temperature, without any actual facts against it being brought forward. In my paper on the conductivity of electrolytes I was led to the conclusion that at the most extreme dilutions all salts would consist of simple conducting molecules. But the conducting molecules are, according to the hypothesis of Clausius and Williamson, dissociated; hence at extreme dilutions all salt molecules are completely dissociated. The degree of dissociation can be simply found on this assumption by taking the ratio of the molecular conductivity of the solution in question to the molecular conductivity at the most extreme dilution." These two short excerpts give the gist of the complete theory.

Van 't Hoff and Arrhenius now made their ideas available to a wider public by publishing them in the first volume of the *Zeitschrift für physikalische Chemie* in the latter half of 1887. Van 't Hoff accepts Arrhenius's theory for electrolytes and adds finally

Avogadro's Law to those of Boyle and Charles as being applicable to dilute solutions. Arrhenius gives the relationship between van 't Hoff's constant i and the degree of dissociation α in the form

$$i = 1 + (k - 1)\alpha$$

where k is the number of ions into which the molecule of the electrolyte dissociates, *e.g.*, 2 for KCl, 3 for K_2SO_4. He compares the values of i calculated from Raoult's freezing-point data on the one hand, and from the molecular conductivity on the other, for some 80 different substances, and finds a very satisfactory accordance. In the second part of his paper he discusses the properties of electrolytes in aqueous solutions from the point of view of their additive character, which he attributes to the independence of their ions.

The theories of osmotic pressure and of electrolytic dissociation were now fairly launched, and, propelled by the driving-power of Ostwald through the waters of scientific opinion, they soon attained a world-wide recognition, though often meeting very heavy weather. That their reception was so favourable is indeed somewhat surprising, for it must be remembered that in those days the marvels of X-rays, of radioactivity, of wireless transmission, had not prepared the way for that loosening and abandonment of fixed physical ideas to which we are to-day accustomed, if not altogether reconciled. Their general acceptance was largely due to their comparative simplicity. They could be easily tested practically, and little mathematics was required in their development, so that experimental work, centred originally in Ostwald's laboratory, but gradually spreading to others in Germany and abroad, was in the next decade assiduously carried out by a new generation of physical chemists. Their application by Nernst (1889) to electromotive force was an advance of the first order. Arrhenius himself played a principal part in the development. Amongst his important contributions to the subject published in Ostwald's *Zeitschrift* may be mentioned the theory of isohydric solutions (1888), the heat of dissociation of electrolytes and the influence of temperature on the degree of dissociation (1889), the conditions of equilibrium between electrolytes (1890), the determination of electrolytic dissociation of salts from solubility experiments (1893), the hydrolysis of salts of weak acids and weak bases (1894), the alteration of the strength of weak bases by the addition of salts (1899).

At this point it may be well to refer to Arrhenius's position with regard to the problem of the abnormality of strong electrolytes, which, unlike the weak electrolytes, do not conform to Ostwald's dilution-law. Naturally this puzzling exception to the theory he

had put forward constantly claimed his attention. Although he did not succeed in accounting for it, he had arrived at a clear conception of the lines along which a solution might be sought, as may be seen from his book, "Theories of Solution," published in 1912 from the Silliman Lectures delivered at Yale in 1911. He groups the theories which might be brought forward to explain the anomaly under four headings:

1. Change of ionic friction with dilution.
2. Electric attraction of the charges of the ions.
3. Influence of foreign substances on the osmotic pressure (so-called salt-action).
4. Hydration of the ions.

The second of these, with its effect on the first and third, is now recognised as the chief cause of the abnormality. Arrhenius's original theory is sometimes spoken of as entirely obsolete. But it is well to remember that if the younger men of to-day see a little further into the nature of electrolytic solutions than Arrhenius, they do so by standing on Arrhenius's shoulders.

During these years Arrhenius also worked on other physico-chemical subjects, for example, on viscosity of pure liquids and solutions, on conduction in hot gases and flames, on diffusion in aqueous solution, on the velocity of hydrolysis of ethyl acetate and on the inversion of cane-sugar in acid solutions. In a paper on the last subject (1889) Arrhenius makes another theoretical contribution of great significance. He is discussing the effect of temperature on reaction velocity which amounts at the ordinary temperature to an increase of 10 to 15 per cent. for one degree rise. This is much too great to be accounted for by increase of molecular velocity or diminution of viscosity. Besides, the nature of the increase is altogether different from that exhibited in the temperature coefficient of ordinary physical properties. For equal increments of temperature the increase is not approximately arithmetical, but geometrical. This circumstance indicates that the increase in reaction velocity with temperature is not due to change in physical properties of the reacting substances. A similar very rapid change in reaction velocity is observed when ammonium salts are added to ammonia which is saponifying ethyl acetate. Here the explanation is that the ammonium salts greatly reduce the concentration of the free hydroxide ions which really determine the reaction. May we not then surmise that in the inversion of cane-sugar the amount of the really active substances is increased by temperature? The amount of hydrogen-ion, one of the active substances, is little affected by temperature. We must therefore

assume that the other really active substance is not cane-sugar, as this is not changed in amount by temperature, but another hypothetical substance, which is produced from cane-sugar as fast as it is removed by inversion. Arrhenius here reverts to his old distinction between "active" and "inactive" molecules. The hypothetical substance is "active cane-sugar" formed from the inactive substance. It is present at all available temperatures in very minute amount, and the quantity of it in equilibrium with the inactive cane-sugar increases about 12 per cent. per degree. We are therefore dealing principally with the effect of temperature on an *equilibrium*, namely, that between the active and the inactive substance, and can apply van 't Hoff's equilibrium equation

$$d \log_e k/dT = q/2T^2,$$

where k is the equilibrium constant and q is the heat of activation. For a small range of temperature this leads to

$$\log k = C - A/RT,$$

i.e., a straight line should be obtained on Arrhenius's assumption if we plot the logarithm of the velocity coefficient against the reciprocal of the absolute temperature, the slope of the line measuring the heat of activation. Arrhenius's equation actually applies to many homogeneous and heterogeneous reactions, and although there is much that is arbitrary in its derivation, it is in its general character quite in accordance with modern ideas.

Returning once more to his personal fortunes, we find that after 1887 he was recognised abroad as one of the chief figures of physical chemistry, but the death of Edlund in 1888 deprived him of his stoutest champion at home, and greatly reduced his chances of obtaining suitable academic employment in Sweden. Abortive negotiations to establish him in a chair of physics at Utrecht and of chemistry at Graz were succeeded by a definite call to the chair of chemistry at Giessen in 1891. Arrhenius, however, notwithstanding the *invidia inter suos* to which he had been subjected, was intensely patriotic and declined the offer on the chance of being appointed chief of the laboratory of physics in the Högskola (University College) at Stockholm, a post which at this time had become vacant. Arrhenius was successful in his candidature and obtained this lectureship, which was in 1895 converted into a professorship, although once more against formidable opposition, only overcome by the strong backing of German physicists. This chair Arrhenius held till 1905. During the years 1896—1902 he was Rector of the Högskola, and through his personality did much to stabilise and develop the struggling institution notwithstanding

that he had no fondness for administrative tasks. Although his laboratory was small and poorly equipped, the name of Arrhenius was sufficient to attract foreign workers, among whom may be mentioned Abegg, Bredig, Cohen and Euler, who afterwards succeeded him in the chair. Foreign distinctions also began to come his way. He was elected an honorary fellow of this Society in 1898, and was awarded the Davy Medal of the Royal Society in 1902. At last he received recognition, and that of the most handsome description, from his own countrymen by the award of the Nobel Prize for Chemistry in 1903.

His interest had meanwhile been diverted from the study of solutions to other fields of science, at first to cosmic and meteorological problems.

One of his very early papers (1883) dealt with an observation of globe lightning near Upsala, and his work on conducting gases had led him to study electrical phenomena in the earth's atmosphere. With his friend the meteorologist, Nils Ekholm, he investigated the influence of the moon on the electric state of the atmosphere, on the aurora and on thunder-storms. In a long memoir (1896) he attempted to account for the onset and passing of glacial periods by the variation in the amount of carbon dioxide in the atmosphere. This gas exerts a selective absorption, allowing the solar radiation freely to pass inwards, but to a great extent stopping the lower-temperature radiation from the earth outwards. Arrhenius calculated that from this green-house effect the temperature in the arctic regions might rise 8°C if the carbon dioxide content of the atmosphere increased to somewhat more than double its present value, and that in order to get the temperature of an ice-age between the 40th and 50th parallels, the value would have to sink to abont half. The variation in the carbonic acid content he attributed chiefly to variation in volcanic activity. The problem of the Ice Ages is still a vexed question amongst geologists, but Arrhenius made a notable contribution to its discussion.

Another important paper on a geological subject was a theory of vulcanicity based on physico-chemical principles (1900). According to it the sea-floor acts as a kind of semipermeable memhrane, permitting water molecules to pass but not silicate molecules. Water at no very great distance under the surfaee of the crust would be at a temperature above its critical point, and therefore a gas, and would be absorbed by the fluid magma under the great pressures existing. But by extrapolation from known data it may be shown that, although at room temperature water is a much weaker acid than silicic acid, yet at high temperatures the reverse is the case, water at 1000° being probably 80 times stronger than silicic acid.

In the magma, then, water will attack and decompose silicates, and thus be potentially stored up in the form of acid and base. When the magma on rising is cooled, the reverse process takes place; water is liberated and at a certain height will overcome the pressure of the column above it, eject the superincumbent fluid, and cause a volcanic eruption. A volcano thus acts in much the same way as a geyser. The theory aims at explaining the proximate cause of eruptions, and has met with wide acceptance.

In 1898 Arrhenius wrote a remarkable paper on the action of cosmic influences on physiological processes, and in 1903 he surprised his chemical friends by publishing his "Lehrbuch der kosmischen Physik," a work of extraordinary learning and scholarship. In it he passes under review an extensive collection of observational material and deals with it according to his own methods. The most striking novelty of treatment is the use he makes of radiation pressure, the existence of which had been predicted by Clerk Maxwell. It was applied by Arrhenius to various cosmic phenomena even before its experimental confirmation in the laboratory by Nichols and Hull and by Lebedev. Arrhenius calculated that at the surface of the sun the repulsive force of the radiation would balance the sun's gravitational attraction on black particles of diameter about $1{\cdot}5\,\mu$, and specific gravity 1, and that smaller particles than these would be repelled. Schwarzschild made some necessary corrections and showed that the maximum repulsion would be for completely reflecting particles (sp. gr. 1) if their diameter was about $0{\cdot}16\,\mu$, and it would then be 10 times the gravitational attraction. From the sun then we might expect streams of such minute particles to be shot out in all directions. Many of these particles would be electrically charged from the ionisation existing in the sun's gaseous atmosphere. Arrhenius shows how the phenomena of the solar corona, comets, the aurora, and the zodiacal light may be caused or influenced by these particles.

With the beginning of the present century Arrhenius's thoughts took a new turn. He became interested in serum therapy, and in the summer of 1902 he went to work in Ehrlich's laboratory in Frankfort. He collaborated with Thorvald Madsen and published jointly with him in the same year a memoir on the occasion of the opening of the Danish State Serum Institute, of which Madsen had been appointed director. It was entitled "Physical Chemistry applied to Toxins and Antitoxins." Madsen was responsible for the experimental methods, Arrhenius for the theoretical treatment. They maintained that the toxin–antitoxin combination (held by Ehrlich to be a firm chemical union) was in reality reversible, and governed by the ordinary mass-action law. The immunological

phenomenon of antitoxin action was likened to the interaction of a weak acid and a weak base, such as boric acid and ammonia, which only partly neutralise each other. The work constitutes a classical study among the early researches into the underlying nature of immunity phenomena, and contributed to laying the foundation of "immunochemistry," a term first applied by Arrhenius himself to a branch of biological research in which reactions of markedly specific character occur between biological principles of unknown chemical nature. Arrhenius pursued this type of research for a decade, and published two books dealing with it, "Immunochemistry" in 1908, and "Quantitative Laws in Biological Chemistry" in 1915.

In the year 1905 Arrhenius happened to be in Berlin and was asked by the University adviser of the Prussian Ministry of Education if he would be inclined to accept a position in the Prussian Academy, similar to that held by van 't Hoff. This was a very tempting proposal, but Arrhenius, with his usual patriotism, requested time to consider it, and asked and was granted permission to speak of it to the Minister of Education in Sweden. It had been the intention of the Academy of Sciences to found a Nobel Institute for Chemistry and one for Physics, but the wish having been expressed by King Oscar II that Arrhenius should not be allowed to leave Sweden, the Academy resolved to found forthwith, instead of the two proposed institutes, a Nobel Institute for Physical Chemistry, and of this new foundation Arrhenius was appointed director. It was housed at first in temporary quarters in Stockholm, but at Experimentalfältet, a pretty park in the neighbourhood of the town, a small laboratory was erected with an official residence attached. The laboratory was inaugurated in 1909. Here, with an assistant and a few research workers as guests, Arrhenius could work and write under ideal conditions on such problems of physical chemistry, physiological chemistry, immunochemistry, meteorology and cosmic physics as might please him.

The stormy period of Arrhenius's career was now definitely over, and from the time of his appointment to the Nobel Institute life went very smoothly with him. From being a scientific outcast in Sweden he became a scientific oracle, known and respected by all classes of the people.

He himself did little practical work in the new laboratory, but stimulated and encouraged others. One of his chief pleasures was to attend conferences in all countries for the purpose of meeting his scientific colleagues and discussing with them their special problems. He often visited England and was elected a foreign member of the Royal Society in 1911. In 1914 he gave the Faraday

Lecture to our own Society, and the Tyndall Lectures to the Royal Institution.

Arrhenius liked to acquire knowledge at first hand, and visited many laboratories for this purpose. He spent, for example, three weeks in Rutherford's laboratory in Manchester, working at a practical course in radioactivity under Geiger. At the end of a week he had started a research on the solubility of active deposits, and was with difficulty dragged away from his electroscope to witness some of Jacques Loeb's starfish experiments at the Marine Biological Station.

He devoted a large part of the later years of his life to popularising science. A firm believer in progress through enlightenment, he sought to bring a knowledge of scientific fact and method before the general public. His clear and easy style made his books attractive, though the matters dealt with were often in themselves difficult. The first of these books, "Världarnas Utveckling" (Worlds in the Making), which treats in a popular manner some of the subjects of his "Kosmische Physik," had an immediate and world-wide success, being translated into all the important European languages.

Happy in his work and happy in his family life, Arrhenius during his later years radiated contentment. He was twice married—in 1894 to Sofia Rudbeck, and in 1905 to Maria Johansson. By the first marriage he had one son, Olov Vilhelm Arrhenius, who is known for his work in soil science and agricultural botany, and by the second a son and two daughters.

His health remained good until the autumn of 1925, and although he recovered in a remarkable way from the first seizure, he retired from the Directorship of the Nobel Institute in February 1927, when he was granted a full pension and the right to remain in the official residence. On 2 October, 1927, he died after a week's illness, and was buried in Upsala on the eighth of that month after a solemn service in Stockholm on the previous day.

Arrhenius was of the old breed of natural philosophers, a true polyhistor, devoted to science at large. Being endowed with a memory both tenacious and accurate, he had a marvellous command of scientific fact. He was, however, no unimaginative empiric; his synthetic fancy played over the vast store of knowledge and sought relations between apparently isolated regions. In consequence, his original ideas were concerned with borderland sciences—physical chemistry, cosmic physics, geophysics, immunochemistry. The conjunction in him of two special faculties explains the character of much of his work—his aptitude for scientific speculation, and an extraordinary facility in dealing with figures. He loved

statistics and it is recorded of him that as a very small boy he delighted to sit beside his father and help him in casting his laborious accounts. Arrhenius might begin a new line of work by the consideration of tables of numerical data collected by himself or others. He would frame a formula to fit them—an exercise at which he was uncannily expert—and then evolve a physical hypothesis to account for the formula. Or he might start with a bold speculation as to how two entities were related, formulate this relation, and check the formula by means of data of observation or experiment. There was constant interplay between the speculative and the quantitative sides of his mind. I recollect that one day in the laboratory at Leipzig, after a long spell of very arduous experimental work, he downed tools, saying, "I have worked enough; now I must think," and did not reappear in the laboratory for a fortnight. Extreme experimental accuracy he never aimed at, considering it rather a disadvantage in the search for a general law, and he used to boast that he had never performed an exact experiment in his life. But this statement must be taken with a grain of salt. I know that his work at Leipzig was certainly more accurate than that of most of his fellow-workers in the laboratory, although carried out with the simplest possible apparatus.

Arrhenius had nothing academic about him save learning. In person he was stoutly built, blond, blue-eyed and rubicund, a true son of the Swedish countryside. His nature was frank, generous and expansive. He was full of robust vitality and primitive force. He had hearty likes and dislikes, and beneath his inborn geniality and good-humour was a latent combativeness, easily aroused in the cause of truth and freedom.

He was not politically active, but he was fond of discussing the large questions of world politics. He spoke very bitterly of Norway when she broke the union with Sweden, but later admitted that the separation had been best for both countries, and expressed to me the hope that Britain would give Ireland similar complete freedom. The World War he regarded as essentially a struggle between Germany and Britain, and although his greatest scientific friends belonged to the Central Powers, his sympathy was definitely with the Allies.

A word may be said about Arrhenius as a linguist. He held that to speak a foreign language what one wanted was, not so much knowledge, as courage. Being liberally endowed with this latter quality he spoke and wrote many languages with ease and confidence, if not with accuracy. Indeed he considered it a waste of time to acquire the niceties of a language, and was of opinion that there should be a universal language—he suggested a simplified

English. Any shortcomings of accent or idiom in his own English were amply compensated by a Shakespearean richness of vocabulary, which gave extraordinary pith to many of his sayings.

He paid little regard to literature or art, but keenly appreciated natural beauty, especially the gladdening phenomena of spring. His life-long interest in the lovely Northern Dancers and in comets that "brandish their crystal tresses in the sky" had most likely an æsthetic as well as a scientific basis.

Sweden can boast of many eminent names in science, of which two are by common consent of the first magnitude—Linnæus and Berzelius. Since the death of Berzelius she has had no name to rank with these save the name we commemorate to-day—Arrhenius. Yet withal Svante Arrhenius was so simple, so genuine, so human a personality, that those who had the privilege of his intimacy always forgot the great scientific master in the genial companion and the kindly, lovable friend.

CLXXXIII.—*The Dilution and Neutral-salt Errors of Buffer Mixtures.*

By Charles Morton.

Owing to the wide distribution of neutral salts in tissues and body-fluids, the well-known fact that the apparent hydrogen-ion concentration of buffer mixtures is increased on the addition of neutral salts is of especial importance in biochemical investigations. In the case of polybasic buffers, such as the phosphate mixtures, neglect of neutral-salt effects may lead to appreciable error. The problem has been examined, so far as the phosphate mixtures are concerned, by Michaelis and Krüger (*Biochem. Z.*, 1921, **119**, 307), and by Cohn (*J. Amer. Chem. Soc.*, 1927, **49**, 173), but no systematic investigation of the dilution and salt errors of buffer mixtures in general appears to have been undertaken.

The properties of the following mixtures have now been studied: (1) Half-neutralised solutions of acetic and cacodylic acids; (2) one-fourth-neutralised solutions of aspartic acid and of arginine; (3) three-fourths-neutralised solutions of *o*-phthalic and α-monoglycerylphosphoric acids; (4) mixtures of sodium pyrophosphate and hydrochloric acid in the molecular proportions (*a*) 2 : 3, (*b*) 2 : 1. For such mixtures we have, respectively, (1) $p_H = p_K$, (2) $p_H = p_{K_1}$, (3) $p_H = p_{K_2}$, (4*a*) $p_H = p_{K_2}$, (4*b*) $p_H = p_{K_4}$, where $K = 10^{-p_K}$ is the apparent dissociation constant of the buffer electrolyte. To these solutions various amounts of *N*-potassium chloride, *N*-sodium

chloride, $M/3$-potassium sulphate, $M/3$-barium chloride, and $M/4$-magnesium sulphate were added, and the p_H (or p_K) change produced by each addition was noted. The effect of dilution was also studied.

The experimental results are in Tables I–IX. In all cases p_K decreases on the addition of neutral salts, but increases on dilution. Both effects become more strongly marked as the valency of the buffer acid increases. When the concentration of added salt is small, the p_H change is independent of the specific nature of the salt, depending only on the valency type; with larger additions a specific salt action is exhibited. As regards the importance of their effects in inducing p_H change in acid buffer mixtures, the influence of neutral salts is in the order $BaCl_2 > MgSO_4 > NaCl > KCl > K_2SO_4$, whatever the nature of the buffer acid. For basic buffers the order is reversed: $K_2SO_4 > KCl > NaCl$.

In dilute solution, when free acid and salt were present in equivalent concentration, the p_K or p_H changes brought about by further dilution, or by the addition of small quantities of neutral salts, were satisfactorily described by the equation

$$p_k = p_H + A\sqrt{\mu} = p_K + A\sqrt{\mu} \quad . \quad . \quad . \quad . \quad (1)$$

where μ is the ionic strength as defined by Lewis and Randall (*J. Amer. Chem. Soc.*, 1921, **43**, 1112), and p_k and A are true constants. When acid and salt are not present in equivalent concentration, the equation

$$p_k = p_H + \log [\text{acid}]/[\text{salt}] + A\sqrt{\mu} \quad . \quad . \quad . \quad (2)$$

applies within the limits of validity of Henderson's equation (*i.e.*, within the p_H limits 4—10). The numerical value of A is 0·5 for monobasic acids, of the order of 1·5 for dibasic acids, 2·5 for tribasic acids, and, in general, roughly equal to $(n - 0{\cdot}5)$ for an n-valent acid.

In solutions of higher ionic strength, the hydrogen-ion relationships are defined by the expression

$$p_k = p_K + A\sqrt{\mu} - B\mu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$p_k = p_H + \log [\text{acid}]/[\text{salt}] + A\sqrt{\mu} - B\mu \quad . \quad . \quad (4)$$

The constants A and p_k have the same significance and numerical values as before, and B is a coefficient expressing the specific action of the ions. Let the values of p_K in three buffer solutions containing identical ions, but of different ionic strengths μ', μ'', μ''', be $p_{K'}$, $p_{K''}$, and $p_{K'''}$, respectively. Then $p_k = p_{K'} + A\sqrt{\mu'} - B\mu' = p_{K''} + A\sqrt{\mu''} - B\mu'' = p_{K'''} + A\sqrt{\mu'''} - B\mu'''$,

whence $$A = \frac{ac_1 - a_1c}{bc_1 - b_1c} \text{ and } B = \frac{ab_1 - a_1b}{bc_1 - b_1c} \quad . \quad . \quad (5)$$

where $a = p_{K''} - p_{K'}$, $b = \sqrt{\mu'} - \sqrt{\mu''}$, $c = \mu' - \mu''$.
$a_1 = p_{K'''} - p_{K'}$, $b_1 = \sqrt{\mu'} - \sqrt{\mu'''}$, $c_1 = \mu' - \mu'''$.

By means of (5) the values of A and B may be obtained independently of one another, and by substitution in equation (3) p_k is obtained.

By the use of this method, the values of A, B, and p_k given in Tables II—IX were obtained. The constancy of k throughout ranges of dilution and salt concentration varying from $N/2$ to $N/1000$ is in general good, and appears to justify the use of the above method of formulation. The mean values of p_k and the salt coefficient B for the salts and mixtures studied were as follows (C is the molar concentration of the free acid and of the salt):

Buffer electrolyte.		C.	p_k.	Values of B for K_2SO_4.	KCl.	$NaCl$.	$MgSO_4$.	$BaCl_2$.
Aspartic acid	K	0·02	3·895	0·485	0·402	0·252	0·209	0·057
Acetic acid	K	0·01	4·735	0·411	0·348	0·295	0·160	0·148
Cacodylic acid	K	0·04	6·247	0·352	—	0·259	0·119	0·153
Phthalic acid	K_2	0·01	5·333	0·961	0·845	0·759	0·466	0·435
α-Glycerylphosphoric acid	K_2	0·01	6·744	0·965	0·837	0·629	0·288	0·256
Pyrophosphoric acid...	K_3	0·02	6·704	1·48	1·29	0·983		
Pyrophosphoric acid...	K_4	0·02	9·880	1·74	1·33	0·687		
Arginine	K_{B_1}	0·005	5·178	0·371	0·408	0·466		

It is clear that the value of B depends on the specific nature of the salt, and to a less extent on the strength and valency of the buffer acid, decreasing slightly with decreasing strength of the acid and increasing with the valency of the acid.

The Quantitative Expression of Buffer Capacity.

Van Slyke (*J. Biol. Chem.*, 1922, **52**, 525) has suggested as a unit of buffer capacity the differential ratio $\beta = dB/dp_H$, expressing the relationship between the increment dB of strong base and the resulting p_H change. The practical value of a buffer solution depends on the degree of resistance offered to changes in hydrogen-ion concentration occasioned (1) by the presence of acid or basic impurities, (2) by errors of dilution, or by the presence of foreign salts. If trustworthy conclusions as to the reproducibility of a given solution are to be drawn, the magnitude of the errors due to both sources must be known. This point may be illustrated by a comparison of the effects of strong bases and of dilution on the hydrogen-ion concentration of (*a*) 0·1N-sulphuric acid, (*b*) 0·1N-glycine, (*c*) 0·1N-standard acetate.

	(*a*).	(*b*).	(*c*).
p_H change on adding 0·005 equiv. of strong base	0·026	2·48	0·043
p_H change on ten-fold dilution	0·88	0·059	0·061
$\beta = \Delta B/\Delta p_H$	0·19	0·002	0·12
$\pi' = \Delta p_H/\Delta C$	−9·8	−0·66	−0·68

The dilution error (provisionally formulated as $\pi' = \Delta p_H/\Delta C$) involved in the preparation of $0{\cdot}1N$-sulphuric acid is 14 times as great as that of standard acetate; this accounts for the experimental observation that, whereas the former solution has the higher β value, the latter is the more readily reproduced. On the other hand, although $0{\cdot}1N$-glycine and $0{\cdot}1N$-standard acetate have approximately the same dilution errors, the alkali-resisting capacity of standard acetate is 60 times as great as that of the glycine. Of the three solutions, only standard acetate fulfils the requirements of an ideal buffer solution, combining a high β value with a low π' or dilution error.

It appears desirable to supplement the β value of van Slyke by a second unit which will serve as a criterion of the probable dilution or salt error. It has been shown above that in the case of typical buffer mixtures, *i.e.*, mixtures prepared from acids or bases the dissociation constants of which lie between the limits 10^{-4} and 10^{-10}, the dilution and salt errors are functions of the ionic strength rather than of concentration. The proposed unit will be defined, therefore, as the differential ratio $\pi = dp_H/d\sqrt{\mu}$. When both the β and π values of a solution are stated, the buffer efficiency is completely defined: the higher the β value, and the lower the π value, the greater the efficiency.

For a typical buffer mixture within the range of validity of Henderson's equation, we have, from (4),

$$\pi = dp_H/d\sqrt{\mu} = 2B\sqrt{\mu} - A \quad . \quad . \quad . \quad . \quad (6)$$

since the values of p_k and the ratio of acid to salt are inappreciably affected by dilution or by the addition of neutral salts.

In solutions of low ionic strength ($\mu < 0{\cdot}01$), *e.g.*, in dilute buffer solutions, (6) reduces to

$$\pi = -A = 0{\cdot}5 - n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

From equations (6) and (7) it can be deduced that:

(1) The dilution error, unlike the β value, is independent of the strength of the buffer electrolyte.

(2) The limiting dilution error is the same for all mixtures of the same salt and acid, *e.g.*, all the phosphate mixtures of Clark and Lubs have the same limiting dilution error.

(3) All buffer mixtures prepared from monobasic acids or monoacid bases have the same limiting dilution error, *viz.*, $-0{\cdot}5$.

(4) The limiting dilution error rapidly increases with the valency of the buffer acid or base. For dibasic acids, *e.g.*, the phthalate and phosphate mixtures, the error is 3 times as great as for monobasic acid mixtures. Hence, *ceteris paribus*, monobasic buffer mixtures are preferable to polybasic mixtures.

TABLE I.

Buffer electrolyte.	A.	C.	$\sqrt{\mu}$.*	$E.M.F.$	p_H.	K.	k.
Aspartic acid † .... K_1	0·5	0·02	0·142	0·4721	3·682	$1{\cdot}5\times10^{-4}$	$1{\cdot}27\times10^{-4}$
		0·01	0·101	0·4748	3·878	1·4	1·21
		0·005	0·072	0·4757	3·892	1·3	1·24
		0·0025	0·051	0·4782	3·933	1·3	1·26
		0·00125	0·037	0·4793	3·952	1·3	1·28
Cacodylic acid .... K	0·5	0·04	0·200	0·6116	6·153	$7{\cdot}0\times10^{-7}$	$5{\cdot}6\times10^{-7}$
		0·02	0·141	0·6123	6·165	6·8	5·8
		0·01	0·100	0·6135	6·184	6·5	5·8
		0·005	0·0707	0·6144	6·198	6·3	5·8
		0·0025	0·050	0·6145	6·200	6·3	5·9
		0·00125	0·035	0·6150	6·209	6·2	5·9
Phthalic acid .... K_2	1·5	0·010	0·200	0·5476	5·055	$8{\cdot}8\times10^{-6}$	$4{\cdot}4\times10^{-6}$
		0·005	0·141	0·5502	5·098	8·0	4·9
		0·0025	0·100	0·5535	5·158	7·0	5·0
		0·00125	0·071	0·5543	5·166	6·8	5·3
		0·000625	0·050	0·5584	5·235	5·8	4·9
Glycerylphosphoric acid K_2	1·5	0·01	0·200	0·6296	6·452	$3{\cdot}5\times10^{-7}$	$1{\cdot}8\times10^{-7}$
		0·005	0·141	0·6330	6·509	3·1	1·9
		0·0025	0·100	0·6348	6·539	3·9	2·0
		0·00125	0·0707	0·6385	6·601	2·5	2·0
Pyrophosphoric acid (i) K_3	2·5	0·02	0·490	0·5022	5·707	$16{\cdot}0\times10^{-7}$	$0{\cdot}95\times10^{-7}$
		0·01	*0·346*	*0·6012*	*5·947*	*11·3*	*1·5*
		0·005	0·245	0·6066	6·037	9·2	2·2
		0·0025	0·173	0·6148	6·173	6·7	2·5
		0·00125	0·123	0·6198	6·256	5·5	2·7
Pyrophosphoric acid (ii) K_4	3·5	0·02	0·583	0·7410	8·307	40×10^{-10}	$0{\cdot}45\times10^{-10}$
		0·01	0·412	0·7520	8·489	32	1·2
		0·005	0·292	0·7626	8·664	22	2·1
		0·0025	0·206	0·7673	8·744	18	3·4
		0·00125	0·146	0·7723	8·826	15	4·6

* *From the definition of* Lewis and Randall, *it follows that the ionic strengths of solutions* of uni-bivalent, uni-tervalent, and uni-quadrivalent electrolytes are respectively equal to three, six, and ten times the molar concentrations, and that of a uni-univalent electrolyte is equal to the normality. The ionic strengths of the various mixtures were therefore derived as follows

Arginine and aspartic, acetic, and cacodylic acid mixtures: $\mu = [\text{salt}] = C$.

Phthalic and glycerylphosphoric mixtures: $\mu = [HA'] + 3[A''] = 4C$, where $C = [HA'] = [A'']$.

Pyrophosphoric mixture (i): $\mu = 6[HP_2O_7'''] + 3[H_2P_2O_7''] + [Cl'] = 12C$, where $C = [HP_2O_7'''] = [H_2P_2O_7''] = \frac{1}{2}[Cl']$.

Pyrophosphoric mixture (ii): $\mu = 10[P_2O_7''''] + 6[HP_2O_7'''] + [Cl'] = 17C$, where $C = [P_2O_7''''] = [HP_2O_7'''] = [Cl']$.

† In computing K_1, the expression $p_{K_1} = p_H + \log([\text{salt}] - [H^\cdot])/([\text{salt}] + [H^\cdot])$ was used, the Henderson equation being inexact when $[H^\cdot] > 10^{-4}$.

(5) When $\sqrt{\mu} < A/2B$, $dp_H/d\sqrt{\mu}$ has a negative value, the p_H value of the solution decreasing with increasing ionic strength. When $\sqrt{\mu} = A/2B$, $dp_H/d\sqrt{\mu} = 0$, and, from (4), the corresponding value of the hydrogen-ion concentration, the lowest which can be obtained with a given buffer mixture, is given by $p_H = p_k - \log[\text{acid}]/[\text{salt}] - A^2/4B$. When $\sqrt{\mu} > A/2B$, the p_H value of the mixture increases with increasing ionic strength.

(6) The π–$\sqrt{\mu}$ graph is a straight line, the slope of which is equal to $2B$.

The Thermodynamical Significance of the Dilution and Salt Errors.

Henderson's equation is derived on the assumptions that (1) the concentrations of hydrogen and hydroxyl ions are negligibly small compared with those of the total acid and base; (2) the salt is completely dissociated; (3) the law of mass action, as ordinarily defined in concentration terms, is obeyed. Between the p_H limits

Table II.

Aspartic acid mixture.

$[H_2A] = [HA'] = 0{\cdot}02.$

Salt.	A.	B.	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·020	0·0485	0·0667	0·1091	0·1478	0·1834	0·2462
N-KCl	0·497	0·402	E.M.F.	0·4721	0·4712	0·4707	0·4698	0·4690	0·4686	0·4680
			p_H	3·832	3·818	3·809	3·794	3·781	3·774	3·764
			$K \times 10^4$	1·47	1·52	1·55	1·61	1·66	1·68	1·72
			$k \times 10^4$	1·28	1·24	1·22	1·22	1·22	1·22	1·22
N-NaCl	0·495	0·252	E.M.F.	0·4721	0·4701	0·4699	0·4685	0·4675	0·4667	0·4656
			p_H	3·832	3·799	3·796	3·772	3·756	3·743	3·724
			$K \times 10^4$	1·47	1·59	1·60	1·69	1·75	1·81	1·89
			$k \times 10^4$	1·27	1·27	1·24	1·24	1·23	1·23	1·24
$M/3$-K_2SO_4	0·499	0·485	E.M.F.	0·4721	0·4718	0·4715	0·4712	0·4710	0·4705	0·4704
			p_H	3·832	3·827	3·822	3·818	3·815	3·806	3·805
			$K \times 10^4$	1·47	1·49	1·51	1·52	1·53	1·56	1·57
			$k \times 10^4$	1·28	1·22	1·21	1·18	1·16	1·17	1·16
$M/3$-$BaCl_2$	0·498	0·057	E.M.F.	0·4721	0·4695	0·4685	0·4661	0·4646	0·4634	0·4614
			p_H	3·832	3·788	3·772	3·733	3·708	3·688	3·655
			$K \times 10^4$	1·47	1·63	1·69	1·85	1·96	2·05	2·21
			$k \times 10^4$	1·26	1·27	1·37	1·28	1·28	1·29	1·29
$M/4$-$MgSO_4$	0·500	0·209	E.M.F.	0·4721	0·4710	0·4700	0·4682	0·4670	0·4668	0·4652
			p_H	3·832	3·815	3·797	3·768	3·748	3·736	3·718
			$K \times 10^4$	1·47	1·53	1·60	1·71	1·79	1·84	1·91
			$k \times 10^4$	1·26	1·22	1·22	1·23	1·23	1·23	1·22
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·3000	0·3467	0·3875	0·4235	0·4556	0·4842	0·5100
N-KCl	0·497	0·402	E.M.F.	0·4678	0·4677	0·4675	0·4674	0·4674	0·4673	0·4672
			p_H	3·761	3·759	3·756	3·755	3·755	3·753	3·752
			$K \times 10^4$	1·73	1·74	1·75	1·76	1·76	1·77	1·77
			$k \times 10^4$	1·22	1·22	1·25	1·23	1·23	1·25	1·25
N NaCl	0·495	0·252	E.M.F.	0·4647	0·4642	0·4639	0·4636	0·4633	0·4630	0·4627
			p_H	3·710	3·701	3·697	3·691	3·686	3·681	3·676
			$K \times 10^4$	1·95	1·99	2·01	2·04	2·06	2·08	2·11
			$k \times 10^4$	1·24	1·24	1·24	1·24	1·24	1·25	1·26
$M/3$ K_2SO_4	0·499	0·485	E.M.F.	0·4704	0·4703	0·4703	0·4704	0·4703	0·4702	0·4701
			p_H	3·805	3·803	3·803	3·805	3·803	3·801	3·799
			$K \times 10^4$	1·57	1·57	1·57	1·57	1·57	1·58	1·59
			$k \times 10^4$	1·16	1·18	1·19	1·19	1·21	1·22	1·23
$M/3$-$BaCl_2$	0·498	0·057	E.M.F.	0·4603	0·4592	0·4585	0·4577	0·4568	0·4567	0·4563
			p_H	3·637	3·618	3·607	3·593	3·578	3·576	3·570
			$K \times 10^4$	2·31	2·41	2·47	2·55	2·64	2·66	2·69
			$k \times 10^4$	1·28	1·28	1·27	1·28	1·39	1·27	1·27
$M/4$-$MgSO_4$	0·500	0·209	E.M.F.		0·4639	0·4632	0·4626	0·4623	0·4618	0·4617
			p_H		3·697	3·684	3·674	3·669	3·661	3·659
			$K \times 10^4$		2·01	2·07	2·12	2·14	2·18	2·19
			$k \times 10^4$		1·21	1·22	1·23	1·23	1·24	1·23

Mean value of $k_A = 1{\cdot}27 \times 10^{-4}$.

4—10 the first assumption is obviously justified at ordinary concentrations. If the second and third assumptions were both valid, therefore, dilution and neutral salt errors would be non-existent. The fact that both errors are functions of the ionic strength rather than of concentration suggests that it is the third assumption which is at fault, and that the activity concept may offer a solution. The introduction of the activity correction into the Henderson equation leads to the expression

$$p_k = p_H + \log\,[\text{acid}]/[\text{salt}] + \log f_a/f_s \qquad (8)$$

in which f_a and f_s are the activity coefficients of the undissociated acid and of the salt anions, or of the acid anions of lower and higher valency, respectively, and $k = 10^{-p_k}$ is a true constant, the thermodynamic dissociation constant. Brønsted (*Trans. Faraday Soc.*,

TABLE III.

Acetic acid mixture.

[HA] = [A′] = 0·01.

Salt.	A.	B.	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·010	0·0388	0·0571	0·100	0·1391	0·1760	0·2385
$M/3\text{-}BaCl_2$	0·5	0·148	*E.M.F.*	0·5233	0·5204	0·5197	0·5177	0·5163	0·5153	0·5138
			p_H	4·684	4·635	4·624	4·591	4·567	4·551	4·527
			$K \times 10^5$	2·07	2·32	2·38	2·56	2·71	2·81	2·97
			$k \times 10^5$	1·85	1·87	1·84	1·85	1·85	1·85	1·83
$N\text{-}NaCl$	0·5	0·295	*E.M.F.*	0·5233	0·5200	0·5190	0·5179	0·5170	0·5164	0·5154
			p_H	4·684	4·629	4·613	4·594	4·580	4·569	4·553
			$K \times 10^5$	2·07	2·35	2·44	2·55	2·63	2·70	2·80
			$k \times 10^5$	1·86	1·92	1·92	1·90	1·88	1·88	1·87
$M/3\text{-}K_2SO_4$	0·5	0·411	*E.M.F.*	0·5233	0·5213	0·5210	0·5200	0·5193	0·5187	0·5183
			p_H	4·684	4·650	4·646	4·629	4·616	4·608	4·601
			$K \times 10^5$	2·07	2·24	2·26	2·35	2·42	2·47	2·51
			$k \times 10^5$	1·86	1·85	1·81	1·80	1·80	1·80	1·79
$N\text{-}KCl$	0·5	0·348	*E.M.F.*	0·5233	0·5210	0·5205	0·5194	0·5188	0·5182	0·5176
			p_H	4·684	4·646	4·637	4·619	4·610	4·599	4·588
			$K \times 10^5$	2·07	2·26	2·31	2·40	2·46	2·52	2·58
			$k \times 10^5$	1·86	1·86	1·83	1·81	1·78	1·79	1·78
$M/4\text{-}MgSO_4$	0·5	0·160	*E.M.F.*	0·5233	0·5200	0·5192	0·5179	0·5170	0·5160	0·5145
			p_H	4·684	4·629	4·616	4·594	4·580	4·563	4·538
			$K \times 10^5$	2·07	2·35	2·42	2·55	2·63	2·74	2·90
			$k \times 10^5$	1·85	1·90	1·88	1·84	1·80	1·80	1·80
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·2928	0·3401	0·3813	0·4176	0·4501	0·4790	0·5050
$M/3\text{-}BaCl_2$	0·5	0·148	*E.M.F.*	0·5127	0·5119	0·5110	0·5105	0·5100	0·5097	0·5093
			p_H	4·508	4·494	4·480	4·471	4·463	4·458	4·451
			$K \times 10^5$	3·11	3·21	3·31	3·38	3·44	3·48	3·54
			$k \times 10^5$	1·84	1·84	1·85	1·85	1·85	1·85	1·85
$N\text{-}NaCl$	0·5	0·295	*E.M.F.*	0·5148	0·5142	0·5138	0·5135	0·5130		
			p_H	4·543	4·533	4·527	4·522	4·513		
			$K \times 10^5$	2·86	2·93	2·97	3·01	3·07		
			$k \times 10^5$	1·87	1·88	1·89	1·89	1·92		
$M/3\text{-}K_2SO_4$	0·5	0·411	*E.M.F.*	0·5180	0·5179	0·5178	0·5176	0·5176	0·5175	0·5175
			p_H	4·596	4·594	4·593	4·588	4·588	4·587	4·587
			$K \times 10^5$	2·54	2·55	2·55	2·58	2·58	2·59	2·59
			$k \times 10^5$	1·79	1·80	1·80	1·80	1·82	1·84	1·84
$N\text{-}KCl$	0·5	0·348	*E.M.F.*	0·5172	0·5170	0·5168	0·5156	0·5155	0·5153	0·5153
			p_H	4·582	4·580	4·576	4·556	4·555	4·551	4·551
			$K \times 10^5$	2·62	2·63	2·66	2·78	2·79	2·81	2·81
			$k \times 10^5$	1·77	1·76	1·77	1·84	1·85	1·86	1·86
$M/4\text{-}MgSO_4$	0·5	0·160	*E.M.F.*	0·5134	0·5125	0·5118	0·5110	0·5104	0·5098	0·5093
			p_H	4·520	4·505	4·493	4·480	4·469	4·460	4·451
			$K \times 10^5$	3·02	3·13	3·21	3·31	3·40	3·47	3·54
			$k \times 10^5$	1·80	1·81	1·82	1·83	1·85	1·87	1·88

Mean value of $k = 1{\cdot}84 \times 10^{-5}$.

1927, **23**, 418) puts the Debye–Hückel (*Physikal. Z.*, 1923, **24**, 185) equation for the activity coefficient f of an ion of valency z in the form $-\log f = 0{\cdot}5z^2\sqrt{\mu} + b\mu$. For the n-th stage in the dissociation of a weak acid this gives $-\log f_a = 0{\cdot}5(n-1)^2\sqrt{\mu} + b'\mu$ and $-\log f_s = 0{\cdot}5n^2\sqrt{\mu} + b''\mu$, or $\log f_a/f_s = (n - 0{\cdot}5)\sqrt{\mu} - B\mu$, where $B = b' - b''$.

Equations (8) and (4), therefore, are identical and the data of Tables I—IX constitute an experimental verification of the Debye–Hückel theory.

For mono- and di-basic acids, the numerical values of the proportionality constant A are in excellent agreement with those derived thermodynamically from the Debye–Hückel theory, *viz.*, 0·5 and 1·5, respectively, but for acids of higher valency there is

TABLE IV.

Cacodylic acid mixture.

$[HA] = [A'] = 0·04$.

Salt.	A.	B.	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·0400	0·068	0·0857	0·1273	0·1652	0·200	0·2616
N-NaCl	0·5	0·259	$E.M.F.$	0·6116	0·6100	0·6095	0·6089	0·6080	0·6073	0·6065
			p_H	6·153	6·127	6·119	6·108	6·094	6·081	6·068
			$K \times 10^7$	7·0	7·5	7·6	7·8	8·1	8·3	8·6
			$k \times 10^7$	5·7	5·7	5·7	5·6	5·6	5·6	5·6
$M/3$-K_2SO_4	0·5	0·352	$E.M.F.$	0·6116	0·6103	0·6100	0·6094	0·6092	0·6083	0·6079
			p_H	6·153	6·131	6·127	6·116	6·113	6·098	6·091
			$K \times 10^7$	7·0	7·4	7·5	7·7	7·7	8·0	8·1
			$k \times 10^7$	5·8	5·8	5·7	5·6	5·5	5·6	5·6
$M/3$-$BaCl_2$	0·5	0·153	$E.M.F.$	0·6116	0·6101	0·6094	0·6079	0·6068	0·6061	0·6047
			p_H	6·153	6·128	6·116	6·091	6·073	6·061	6·039
			$K \times 10^7$	7·0	7·4	7·7	8·1	8·5	8·7	9·1
			$k \times 10^7$	5·7	5·6	5·6	5·6	5·6	5·6	5·6
$M/4$-$MgSO_4$	0·5	0·119	$E.M.F.$	0·6116	0·6090	0·6082	0·6067	0·6059	0·6050	0·6033
			p_H	6·153	6·110	6·096	6·071	6·057	6·043	6·015
			$K \times 10^7$	7·0	7·8	8·0	8·5	8·8	9·1	9·7
			$k \times 10^7$	5·6	5·8	5·8	5·8	5·8	5·7	5·8
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·3143	0·3601	0·400	0·4352	0·4667	0·4948	0·5200
N-NaCl	0·5	0·259	$E.M.F.$	0·6055	0·6050	0·6048	0·6043	0·6040	0·6038	0·6036
			p_H	6·052	6·043	6·039	6·032	6·027	6·023	6·020
			$K \times 10^7$	8·9	9·1	9·1	9·3	9·4	9·5	9·6
			$k \times 10^7$	5·6	5·6	5·6	5·6	5·7	5·7	5·7
$M/3$-K_2SO_4	0·5	0·352	$E.M.F.$	0·6079	0·6078	0·6070	0·6063	0·6062	0·6061	0·6060
			p_H	6·091	6·089	6·077	6·004	6·063	6·061	6·060
			$K \times 10^7$	8·1	8·1	8·4	8·6	8·7	8·7	8·7
			$k \times 10^7$	5·5	5·5	5·6	5·7	5·7	5·8	5·8
$M/3$-$BaCl_2$	0·5	0·153	$E.M.F.$	0·6037	0·6028	0·6022	0·6015	0·6012	0·6009	0·6004
			p_H	6·022	6·006	5·990	5·985	5·980	5·974	5·968
			$K \times 10^7$	9·5	9·9	10·1	10·4	10·5	10·6	10·8
			$k \times 10^7$	5·6	5·6	5·6	5·6	5·6	5·6	5·6
$M/4$-$MgSO_4$	0·5	0·119	$E.M.F.$	0·6025	0·6011	0·6008	0·6002	0·5995	0·5988	0·5986
			p_H	6·002	5·978	5·973	5·964	5·953	5·940	5·936
			$K \times 10^7$	10·0	10·5	10·6	10·9	11·1	11·5	11·6
			$k \times 10^7$	5·7	5·8	5·7	5·7	5·8	5·8	5·8

Mean value of $k = 5·66 \times 10^{-7}$.

only rough correspondence between the two values. Moreover, the above considerations apply only to weak electrolytes, the dissociation constants of which lie within the limits 10^{-4} and 10^{-9} or 10^{-10}. In any attempt to formulate the dilution errors of strong electrolytes, or of the strongly hydrolysed salts of very weak electrolytes, the effects of changing concentration, as well as of changing ionic strength, must be taken into account. For such electrolytes, the dilution error may be provisionally formulated as $\pi' = \Delta p_H / \Delta C$, and determined experimentally.

EXPERIMENTAL.

The hydrogen electrode was used in conjunction with a saturated calomel half-cell, and with saturated potassium chloride solution as the junction liquid. The temperature was maintained at 30° by circulating water from an electrically controlled thermostat, by means of an "Albany" pump, through jackets surrounding the two electrode vessels.

TABLE V.

Arginine mixture.

[BOH] = [B·] = 0·00545.

Salt.	*A*.	*B*.	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·00545	0·0344	0·0528	0·0959	0·1351	0·1712	0·2350
N-KCl	0·5	0·408	*E.M.F.*	0·7629	0·7672	0·7681	0·7690	0·7695	0·7698	0·7705
			p_H	8·569	8·640	8·654	8·670	8·678	8·684	8·690
			$K \times 10^6$	7·0	8·2	8·5	8·8	9·0	9·1	9·4
			$k \times 10^6$	6·4	6·9	6·9	6·8	6·7	6·6	6·7
M/3-K_2SO_4	0·5	0·371	*E.M.F.*	0·7629	0·7683	0·7693	0·7707	0·7717	0·7726	0·7730
			p_H	8·569	8·658	8·674	8·698	8·714	8·730	8·738
			$K \times 10^6$	7·0	8·6	8·9	9·4	9·8	10·1	10·3
			$k \times 10^6$	6·4	7·1	7·1	7·1	7·2	7·3	7·2
N-NaCl	0·5	0·466	*E.M.F.*	0·7629	0·7646	0·7656	0·7660	0·7667	0·7670	0·7674
			p_H	8·569	8·596	8·614	8·620	8·632	8·638	8·644
			$K \times 10^6$	7·0	7·4	7·8	7·9	8·1	8·2	8·3
			$k \times 10^6$	6·5	6·2	6·3	6·1	6·1	6·1	6·1
M/4-$MgSO_4$			*E.M.F.*	0·7629	0·7641	0·7643	0·7638	0·7626	0·7615	0·7593
			p_H	8·569	8·588	8·590	8·582	8·565	8·545	8·507
M/3-$BaCl_2$			*E.M.F.*	0·7629	0·7631	0·7634	0·7633	0·7628	0·7619	0·7597
			p_H	8·569	8·572	8·576	8·574	8·567	8·553	8·515
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·2896	0·3370	0·3784	0·4149	0·4475	0·4766	0·5027
N-KCl	0·5	0·408	*E.M.F.*	0·7708	0·7708	0·7710	0·7710	0·7710	0·7710	0·7710
			p_H	8·700	8·700	8·704	8·704	8·704	8·704	8·704
			$K \times 10^6$	9·4	9·4	9·5	9·5	9·5	9·5	9·5
			$k \times 10^6$	6·7	6·6	6·7	6·7	6·7	6·7	6·7
M/3-K_2SO_4	0·5	0·371	*E.M.F.*	0·7735	0·7736	0·7734	0·7730	0·7730	0·7729	0·7731
			p_H	8·746	8·748	8·744	8·738	8·738	8·736	8·738
			$K \times 10^6$	10·5	10·5	10·5	10·3	10·3	10·3	10·3
			$k \times 10^6$	7·2	7·2	7·1	7·0	7·0	7·0	7·0
N-NaCl	0·5	0·466	*E.M.F.*	0·7672	0·7678	0·7682	0·7675	0·7677	0·7672	0·7672
			p_H	8·640	8·650	8·656	8·646	8·650	8·640	8·640
			$K \times 10^6$	8·2	8·4	8·5	8·3	8·4	8·2	8·2
			$k \times 10^6$	6·0	6·2	6·3	6·2	6·3	6·2	6·2
M/4 $MgSO_4$			*E.M.F.*	0·7572		0·7538	0·7520	0·7503	0·7485	0·7468
			p_H	8·472		8·418	8·387	8·358	8·318	8·301
M/3-$BaCl_2$			*E.M.F.*	0·7560	0·7535	0·7521	0·7510	0·7502	0·7496	0·7495
			p_H	8·465	8·412	8·389	8·371	8·356	8·347	8·345

Mean value of k_{B_1} = 6·64 × 10^{-6}.

(1) *Dilution Experiments.*

In these experiments (Table I) each solution was prepared by mixing 50 c.c. of the previous dilution with an equal volume of water, the same pipette being used.

The values of *k*, the thermodynamic dissociation constant, given in the last column of Table I, are those deduced from the limiting equation (1). At the highest dilutions studied (about *M*/1,000), the experimental error is necessarily somewhat large; it may be claimed, nevertheless, that the Debye–Hückel theory satisfactorily describes the hydrogen-ion relationships of mono- and di-basic mixtures over a wide range of concentration. For mixtures prepared from acids of higher valency, such as the pyrophosphate mixtures, the lack of constancy of *k* indicates that the use of the Debye–Hückel equation is justifiable only as a first approximation.

(2) *Neutral-salt Experiments.*

To 10 c.c. of the mixture under examination, successive small increments of *N*-potassium chloride, *N*-sodium chloride, *M*/3-

Table VI.

Phthalic acid mixture.

$[HA'] = [A''] = 0·01.$

Salt.	A.	B.	C.c. added	0·5	1·0	1·5	2·0	3·0	4·0
			μ	0·0857	0·1273	0·1652	0·2000	0·2616	0·3143
N-NaCl	1·5	0·759	*E.M.F.*	0·5414	0·5380	0·5353	0·5331	0·5302	0·5280
			p_H	4·952	4·895	4·851	4·814	4·766	4·730
			$K_2 \times 10^6$	11·2	12·7	14·1	15·4	17·1	18·6
			$k_2 \times 10^6$	4·7	4·7	4·6	4·6	4·6	4·7
$M/3$-K_2SO_4	1·5	0·961	*E.M.F.*	0·5426	0·5400	0·5378	0·5363	0·5345	0·5330
			p_H	4·972	4·928	4·891	4·867	4·838	4·818
			$K_2 \times 10^6$	10·7	11·8	12·9	13·6	14·5	15·4
			$k_2 \times 10^6$	4·7	4·6	4·6	4·5	4·4	4·4
M-$BaCl_2$	1·5	0·435	*E.M.F.*	0·5337	0·5248	0·5201	0·5162	0·5116	0·5086
			p_H	4·823	4·677	4·597	4·533	4·457	4·407
			$K_2 \times 10^6$	15·0	21·0	25·3	29·3	34·9	39·2
			$k_2 \times 10^6$	5·9	6·9	7·3	7·6	7·7	7·8
N-KCl	1·5	0·845	*E.M.F.*	0·5417	0·5389	0·5365	0·5340	0·5315	0·5294
			p_H	4·957	4·910	4·871	4·828	4·787	4·752
			$K_2 \times 10^6$	11·0	12·3	13·5	14·9	16·3	17·7
			$k_2 \times 10^6$	5·2	4·6	4·6	4·7	4·6	4·7
$M/4$-$MgSO_4$	1·5	0·466	*E.M.F.*	0·5373	0·5326	0·5290	0·5263	0·5225	0·5199
			p_H	4·884	4·806	4·745	4·700	4·637	4·594
			$K_2 \times 10^6$	13·1	15·6	18·0	20·0	23·1	25·5
			$k_2 \times 10^6$	5·2	5·2	5·3	5·3	5·2	5·2
			C.c. added	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·3601	0·4000	0·4352	0·4667	0·4948	0·5200
N-NaCl	1·5	0·759	*E.M.F.*	0·5266	0·5256	0·5246	0·5232	0·5227	0·5220
			p_H	4·706	4·689	4·673	4·649	4·640	4·629
			$K_2 \times 10^6$	19·7	20·5	21·2	22·4	22·9	23·5
			$k_2 \times 10^6$	4·6	4·6	4·6	4·8	4·8	4·8
$M/3$-K_2SO_4	1·5	0·961	*E.M.F.*	0·5320	0·5310	0·5306	0·5300	0·5292	0·5290
			p_H	4·796	4·779	4·773	4·762	4·749	4·745
			$K_2 \times 10^6$	16·0	16·6	16·9	17·3	17·8	18·0
			$k_2 \times 10^6$	4·5	4·5	4·5	4·6	4·7	4·7
$M/3$-$BaCl_2$	1·5	0·435	*E.M.F.*	0·5064	0·5049	0·5033	0·5020	0·5012	0·5010
			p_H	4·367	4·344	4·318	4·296	4·284	4·280
			$K_2 \times 10^6$	42·8	45·3	48·1	50·6	52·0	52·5
			$k_2 \times 10^6$	7·8	7·6	7·6	7·6	7·5	7·3
N-KCl	1·5	0·845	*E.M.F.*	0·5280	0·5277	0·5270	0·5264	0·5259	0·5251
			p_H	4·730	4·724	4·713	4·702	4·693	4·680
			$K_2 \times 10^6$	18·6	18·9	19·4	19·9	20·3	20·9
			$k_2 \times 10^6$	4·7	4·6	4·6	4·6	4·7	4·8
$M/4$-$MgSO_4$	1·5	0·466	*E.M.F.*	0·5180	0·5164	0·5150	0·5139	0·5130	0·5121
			p_H	4·563	4·536	4·513	4·494	4·480	4·465
			$K_2 \times 10^6$	27·4	29·1	30·7	32·1	33·1	34·3
			$k_2 \times 10^6$	5·1	5·0	5·0	5·0	4·9	5·0

Mean value of $k_2 = 4·65 \times 10^{-6}$.

potassium sulphate, $M/3$-barium chloride, or $M/4$-magnesium sulphate were added, and the *E.M.F.* at each stage was determined. The salts were Kahlbaum's "for analysis, with certificate of guarantee."

The values of k given in Tables II—IX were computed by means of the expression $p_k = p_H + A\sqrt{\mu} - B\mu$. In general, k is constant within the limits of experimental error, *i.e.*, throughout the range of salt concentrations studied (0·0—0·5N), the activation effect is in accordance with the Debye–Hückel theory. Apparent deviations are met with (*a*) in strongly acid mixtures in the presence of potassium and magnesium sulphates, (*b*) in slightly alkaline mixtures on the addition of magnesium sulphate and barium chloride. It is probable that in these cases we are dealing, not with a simple

TABLE VII.

Glycerylphosphoric acid mixture.

[HA′] = [A′] = 0·01.

Salt.	*A.*	*B.*	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·040	0·0680	0·0857	0·1273	0·1652	0·200	0·2616
N-KCl	1·5	0·837	*E.M.F.*	0·6296	0·6258	0·6240	0·6206	0·6185	0·6170	0·6139
			p_H	6·452	6·369	6·359	6·304	6·268	6·244	6·192
			$K \times 10^7$	3·5	4·1	4·4	5·0	5·4	5·7	6·4
			$k \times 10^7$	1·8	1·9	1·9	1·9	1·8	1·8	1·8
N-NaCl	1·5	0·629	*E.M.F.*	0·6296	0·6254	0·6238	0·6204	0·6174	0·6149	0·6117
			p_H	6·452	6·383	6·357	6·300	6·250	6·209	6·155
			$K \times 10^7$	3·5	4·1	4·4	5·0	5·6	6·2	7·0
			$k \times 10^7$	1·8	1·8	1·8	1·8	1·8	1·8	1·7
M/3-K_2SO_4	1·5	0·965	*E.M.F.*	0·6296	0·6260	0·6250	0·6225	0·6204	0·6194	0·6170
			p_H	6·452	6·392	6·375	6·334	6·299	6·282	6·241
			$K \times 10^7$	3·5	4·1	4·2	4·6	5·0	5·2	5·7
			$k \times 10^7$	1·8	1·9	1·8	1·8	1·8	1·7	1·8
M/3-$BaCl_2$	1·5	0·256	*E.M.F.*	0·6296	0·6190	0·6149	0·6095	0·6044	0·6008	0·5962
			p_H	6·452	6·275	6·207	6·119	6·033	5·973	5·896
			$K \times 10^7$	3·5	5·3	6·2	7·6	9·3	10·6	12·7
			$k \times 10^7$	1·8	2·2	2·4	2·4	2·5	2·6	2·5
M/4-$MgSO_4$	1·5	0·288	*E.M.F.*	0·6296	0·6180	0·6144	0·6062	0·6010	0·5985	0·5935
			p_H	6·452	6·260	6·200	6·064	5·977	5·936	5·852
			$K \times 10^7$	3·5	5·5	6·3	8·6	10·5	11·6	14·1
			$k \times 10^7$	1·8	2·3	2·4	2·7	2·9	2·8	2·8
			C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·3143	0·3601	0·4000	0·4352	0·4667	0·4948	0·5200
N-KCl	1·5	0·837	*E.M.F.*	0·6120	0·6109	0·6099	0·6090	0·6083	0·6075	0·6072
			p_H	6·159	6·142	6·126	6·110	6·099	6·091	6·081
			$K \times 10^7$	6·9	7·2	7·5	7·8	8·0	8·1	8·3
			$k \times 10^7$	1·9	1·8	1·9	1·9	1·8	1·8	1·9
N-NaCl	1·5	0·629	*E.M.F.*	0·6089	0·6072	0·6056	0·6043	0·6032	0·6028	0·6020
			p_H	6·108	6·080	6·053	6·032	6·013	6·006	5·994
			$K \times 10^7$	7·8	8·3	8·9	9·3	9·7	9·9	10·1
			$k \times 10^7$	1·8	1·8	1·8	1·8	1·8	1·8	1·8
M/3-K_2SO_4	1·5	0·965	*E.M.F.*	0·6154	0·6142	0·6136	0·6129	0·6128	0·6122	0·6115
			p_H	6·216	6·195	6·186	6·175	6·173	6·163	6·152
			$K \times 10^7$	6·1	6·4	6·5	6·7	6·7	6·9	7·0
			$k \times 10^7$	1·8	1·8	1·8	1·8	1·8	1·8	1·8
M/3-$BaCl_2$	1·5	0·256	*E.M.F.*	0·5921	0·5903	0·5881	0·5855	0·5850	0·5840	0·5829
			p_H	5·829	5·799	5·762	5·719	5·711	5·694	5·676
			$K \times 10^7$	14·8	15·9	17·3	19·1	19·5	20·2	21·1
			$k \times 10^7$	2·6	2·5	2·5	2·5	2·4	2·4	2·4
M/4-$MgSO_4$	1·5	0·288	*E.M.F.*	0·5902	0·5880	0·5862	0·5845	0·5834	0·5825	0·5815
			p_H	5·798	5·761	5·731	5·703	5·684	5·669	5·653
			$K \times 10^7$	15·9	17·3	18·6	19·8	20·7	21·5	22·3
			$k \times 10^7$	2·8	2·8	2·7	2·7	2·7	2·6	2·6

Mean value of $k_2 = 1·80 \times 10^{-7}$.

activation effect, but with a displacement of the acid–base equilibria. Ionic reactions, such as (*a*) $SO_4'' + H^{\cdot} \rightleftharpoons HSO_4'$, (*b*) $Ba^{\cdot\cdot} + OH' \rightleftharpoons Ba(OH)^{\cdot}$, which tend to diminish the hydrogen- (or hydroxyl-) ion concentration, *lead to an alteration of the ratio* [acid]/[salt]. In such circumstances it is no longer correct to assume, *as is done in computing both K and k, that this ratio is* independent of salt concentration.

Conclusions.

(1) The buffer unit of Van Slyke, *viz.*, $\beta = dB/dp_H$, is not in itself a true criterion of buffer efficiency. It is suggested that this value should be supplemented by the unit $\pi = dp_H/d\sqrt{\mu}$ expressing the dilution and neutral-salt errors.

Table VIII.

Pyrophosphoric acid mixture (i).

$[H_2A''] = [HA'''] = 0·02$.

Salt.	A.	B.	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·2400	0·2625	0·2762	0·3093	0·3392	0·3665	0·4156
N-KCl	2·5	1·29	*E.M.F.*	0·5922	0·5886	0·5876	0·5859	0·5845	0·5832	0·5813
			p_H	5·797	5·737	5·720	5·693	5·669	5·646	5·615
			$K_3 \times 10^7$	16·0	18·3	19·1	20·3	21·4	22·6	24·3
			$k_3 \times 10^7$	1·9	2·1	2·1	2·1	2·1	2·1	2·0
N-NaCl	2·5	0·983	*E.M.F.*	0·5922	0·5838	0·5872	0·5846	0·5826	0·5806	0·5776
			p_H	5·797	5·657	5·714	5·670	5·637	5·664	5·554
			$K_3 \times 10^7$	16·0	22·0	19·3	21·4	23·1	24·9	27·9
			$k_3 \times 10^7$	1·6	2·1	1·8	1·8	1·7	1·7	1·7
M/3-K_2SO_4	2·5	1·48	*E.M.F.*	0·5922	0·5911	0·5901	0·5888	0·5878	0·5868	0·5853
			p_H	5·797	5·779	5·762	5·740	5·724	5·707	5·683
			$K_3 \times 10^7$	16·0	16·6	17·3	18·2	18·9	19·6	20·8
			$k_3 \times 10^7$	2·2	2·1	2·2	2·1	2·1	2·1	2·1
M/4-$MgSO_4$			*E.M.F.*	0·5922	0·5735	0·5644	0·5398	0·5250	0·5159	0·5062
			p_H	5·797	5·518	5·333	4·925	4·679	4·528	4·366

Salt.	A.	B.	C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·9
			μ	0·4573	0·4936	0·5250	0·5527	0·5777	0·6003	0·6200
N-KCl	2·5	1·29	*E.M.F.*	0·5798	0·5788	0·5777	0·5769	0·5763	0·5758	0·5753
			p_H	5·590	5·573	5·555	5·543	5·530	5·524	5·516
			$K_3 \times 10^7$	25·7	26·7	27·9	28·6	29·5	29·9	30·5
			$k_3 \times 10^7$	2·0	2·0	2·0	2·0	2·1	2·1	2·1
N-NaCl	2·5	0·983	*E.M.F.*	0·5755	0·5737	0·5718	0·5703	0·5693	0·5683	0·5676
			p_H	5·518	5·489	5·458	5·433	5·417	5·399	5·388
			$K_3 \times 10^7$	30·3	32·4	34·8	36·9	38·3	39·9	40·9
			$k_3 \times 10^7$	1·7	1·7	1·8	1·8	1·8	1·8	1·8
M/3-K_2SO_4	2·5	1·48	*E.M.F.*	0·5843	0·5838	0·5830	0·5825	0·5818	0·5816	0·5807
			p_H	5·666	5·657	5·644	5·635	5·623	5·620	5·606
			$K_3 \times 10^7$	21·6	22·0	22·7	23·2	23·8	24·0	24·8
			$k_3 \times 10^7$	2·1	2·1	2·1	2·1	2·1	2·1	2·2
M/4-$MgSO_4$			*E.M.F.*	0·5004	0·4968	0·4941	0·4921	0·4903	0·4888	0·4873
			p_H	4·270	4·210	4·165	4·132	4·102	4·078	4·061

Mean value of $k_3 = 1·98 \times 10^{-7}$.

Table IX.

Pyrophosphoric acid mixture (ii).

$[HA'''] = [A''''] = 0·02$.

Salt.	A	B.	C.c. added	0·0	0·3	0·5	1·0	1·5	2·0	3·0
			μ	0·3400	0·3598	0·3715	0·4003	0·4262	0·4498	0·4926
N-KCl	3·497	1·33	*E.M.F.*	0·7410	0·7380	0·7369	0·7335	0·7318	0·7292	0·7260
			p_H	8·307	8·256	8·237	8·181	8·153	8·108	8·056
			$K_4 \times 10^{10}$	49·3	55·5	57·9	65·9	70·3	78·0	87·9
			$k_4 \times 10^{10}$	1·3	1·3	1·3	1·4	1·3	1·4	1·4
N-NaCl	3·22	0·687	*E.M.F.*	0·7410	0·7376	0·7358	0·7303	0·7205	0·7237	0·7190
			p_H	8·307	8·249	8·219	8·127	8·063	8·017	7·939
			$K_4 \times 10^{10}$	49·3	56·4	60·4	74·6	86·5	96·2	115·1
			$k_4 \times 10^{10}$	1·1	1·2	1·2	1·3	1·3	1·4	1·4
M/3-K_2SO_4	3·69	1·74	*E.M.F.*	0·7410	0·7392	0·7384	0·7365	0·7349	0·7337	0·7320
			p_H	8·307	8·275	8·262	8·230	8·204	8·185	8·156
			$K_4 \times 10^{10}$	49·3	53·1	54·7	58·9	62·5	65·3	69·8
			$k_4 \times 10^{10}$	1·4	1·4	1·4	1·3	1·3	1·3	1·3

Salt.	A	B.	C.c. added	4·0	5·0	6·0	7·0	8·0	9·0	10·0
			μ	0·5288	0·5604	0·5875	0·6115	0·6332	0·6531	0·6700
N-KCl	3·497	1·38	*E.M.F.*	0·7239	0·7222	0·7207	0·7195	0·7186	0·7178	0·7170
			p_H	8·021	7·991	7·966	7·947	7·930	7·920	7·907
			$K_4 \times 10^{10}$	95·3	102	108	113	118	120	124
			$k_4 \times 10^{10}$	1·4	1·4	1·3	1·3	1·3	1·3	1·3
N-NaCl	3·22	0·687	*E.M.F.*	0·7152	0·7125	0·7103	0·7084	0·7067	0·7052	0·7041
			p_H	7·877	7·830	7·793	7·764	7·756	7·711	7·691
			$K_4 \times 10^{10}$	133	148	161	172	184	195	204
			$k_4 \times 10^{10}$	1·4	1·4	1·4	1·4	1·4	1·4	1·3
M/3 K_2SO_4	3·69	1·74	*E.M.F.*	0·7308	0·7289	0·7282	0·7273	0·7268	0·7263	0·7257
			p_H	8·136	8·104	8·091	8·076	8·069	8·060	8·050
			$K_4 \times 10^{10}$	73·1	78·7	81·1	84·0	85·3	87·1	89·1
			$k_4 \times 10^{10}$	1·3	1·3	1·3	1·3	1·2	1·2	1·2

Mean value of $k_4 = 1·32 \times 10^{-10}$.

(2) The limiting dilution error is independent of the strength and specific nature of the buffer electrolyte, depending only on the valency type.

(3) The limiting dilution error of a monobasic buffer mixture is $\pi = -0{\cdot}5$; that of an n-valent mixture is approximately $(2n - 1)$ times as great.

(4) The neutral-salt error is described by the Debye–Hückel equation in the form $p_k = p_K + A\sqrt{\mu} - B\mu$. The value of A for an n-valent buffer mixture is approximately $(n - 0{\cdot}5)$. The value of B depends on the specific nature of the salt, and on the strength and valency of the buffer electrolyte.

(5) The "thermodynamic dissociation constants" of aspartic (k_{A_1}), acetic, cacodylic, *o*-phthalic (k_2), α-glycerylphosphoric (k_2), and pyrophosphoric (k_3, k_4) acids, and of arginine (k_{B_1}) have been determined.

The author wishes to express his indebtedness to the Principal and Head of the Chemical Department for the provision of facilities, and to Dr. J. C. Crocker for the kind interest he has taken in the work. A grant from the Dixon Fund of the University of London is gratefully acknowledged.

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CLXXXIV.—*The Conductivities of Sodium and Potassium Derivatives of β-Ketonic Compounds in Alcoholic Solution.*

By EILEEN WHITE.

THE molecular conductivities of the sodium and potassium derivatives of ethyl acetoacetate, acetylacetone, benzoylacetone, ethyl *iso*butyl- and *iso*amyl-acetoacetate, and also of sodium and potassium ethoxides and potassium iodide were determined in alcoholic solution at 25° at dilutions of 4 to 1024 litres. The values obtained for greater dilutions show considerable deviations due to the comparatively large errors unavoidable in such dilute solutions.

The measurements were carried out by the usual method with an induction coil and telephone. The alcohol was purified by refluxing with freshly burnt quicklime for 2—3 days, and after distillation had a specific conductivity of $0{\cdot}15 \times 10^{-6}$ mho.

The solutions of the sodium and potassium β-ketonic derivatives were prepared by the addition of the exact amount of alcoholic solution of the corresponding ethoxide of known strength to

slightly more than the theoretical quantity of the ketonic substance also dissolved in alcohol, the solution then being diluted with alcohol to the required volume. Dilution of the solutions during a series of conductivity measurements was effected by pipettes.

Ethyl acetoacetate was purified by washing, drying, and redistillation; b. p. 181°. Ethyl *iso*butylacetoacetate, b. p. 218°, and *iso*amylacetoacetate, b. p. 228°, were prepared by the method of Conrade and Limpach (*Annalen*, 1882, **214**, 137). (The sodio*iso*amyl derivative was found to be optically inactive.) Benzoylacetone after recrystallisation had m. p. 60°. Acetylacetone after drying and redistilling boiled at 137°.

The following tables give the molecular conductivity corresponding to dilution *v*, the values for ethyl sodioacetoacetate in parentheses being those obtained when the solvent contained 5·5% of water.

	$CH_3·CO·CHM·CO·CH_3$,		$C_6H_5·CO·CHM·CO·CH_3$,		$CH_3·CO·CMBu^{\beta}·CO_2Et$,		
v.	M = Na.	M = K.	M = Na.	M = K.	M = Na.	M = K.	KI.
8	5·794	12·096	5·066	10·863	—	—	—
16	8·254	15·43	7·261	13·968	13·293	16·688	24·64
32	11·187	18·89	9·822	17·22	17·155	20·495	27·904
64	14·426	22·234	12·736	20·493	21·427	24·22	32·14
128	18·116	25·68	16·128	24·00	25·754	27·891	35·955
256	21·82	28·672	19·712	26·70	29·939	30·925	39·54
512	25·636	31·565	23·59	29·804	33·485	33·23	42·55
1024	29·927	33·95	27·34	32·307	36·864	35·84	45·261
2048	—	—	—	—	—	—	47·104
4096	—	—	—	—	—	—	47·514

	$CH_3·CO·CM(C_5H_{11})·CO_2Et$,				$CH_3·CO·CMH·CO_2Et$,	
	M = Na.	M = K.	NaOH.	NaOEt.	M = Na.	M = K.
4	—	—	—	—	3·103 (—)	7·0807
8	—	—	—	—	4·712 (7·567)	9·190
16	13·24	16·341	—	—	6·691 (10·688)	12·181
32	17·14	19·85	22·83	20·97	8·96 (14·080)	15·41
64	21·04	23·741	26·40	24·56	12·288 (17·536)	19·09
128	24·038	27·674	30·59	28·15	15·81 (21·376)	23·071
256	27·75	31·232	33·31	31·49	19·71 (25·446)	26·598
512	30·72	34·570	35·43	34·25	24·34 (29·747)	30·37
1024	32·932	36·966	37·89	36·66	28·74 (35·533)	33·38

The experiments show that these substances are conductors of electricity in ethyl-alcoholic solution, the molecular conductivity being only slightly less than that of potassium iodide.

Values for the limiting molecular conductivity at infinite dilution, as found by extrapolation of the curves obtained by plotting the logarithm of the molecular conductivity against the cube root of the concentration (which showed only slight curvature for low concentrations), were seen, when compared amongst themselves, to be inconsistent with the law of independent migration. Thus complete dissociation is not approached at the maximum dilution used (compare Robertson and Acree, *J. Physical Chem.*, 1915, **19**, 381); moreover, the form of the curves indicates that the change in

conductivity with dilution is not wholly due to electrolytic dissociation. It appears likely that there is a certain amount of hydrolysis of the compounds by the traces of water unavoidably present. Whether there is in addition an "alcoholysis," with the formation of sodium ethoxide, could not be determined, for dilute alcoholic solutions of sodium hydroxide and sodium ethoxide show practically the same conductivity.

The author desires to thank Dr. J. C. Crocker for suggesting the subject of this research and for his unfailing interest during its progress.

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CLXXXV.—*Some Thiazole Derivatives. Part II.*

By HERBERT WILLIAM STEPHEN and FORSYTH JAMES WILSON.

IN continuation of Part I (*J.*, 1926, 2531), we have found that diacetophenonethiocarbohydrazone reacts in alcoholic solution in presence of sodium ethoxide with ethyl α-bromopropionate, ethyl α-bromo-*n*-butyrate and ethyl phenylbromoacetate thus,

$$CPhMe{:}N{\cdot}N{:}C(SNa){\cdot}NH{\cdot}N{:}CPhMe + CHRBr{\cdot}CO_2Et =$$
$$\begin{array}{l}CPhMe{:}N{\cdot}N{:}C\text{———}N{\cdot}N{:}CPhMe \\ \qquad\qquad\quad S{\cdot}CHR{\cdot}CO\end{array} + NaBr + EtOH,$$

yielding *3-phenylmethylmethyleneamino-2 : 4-diketo-5-methyl*(or *ethyl*, or *phenyl*)*tetrahydrothiazole-2-phenylmethylmethylenehydrazone* (R = Me, Et, Ph respectively). Unlike the parent compound (R = H), these substances could not be satisfactorily hydrolysed by dilute or concentrated hydrochloric acid and it was not possible to obtain hydrochlorides of the bases (I) or (II), mixtures containing the acids $CHR(SH){\cdot}CO_2H$ invariably resulting.

$$\text{(I.)}\quad \begin{array}{l}NH_2{\cdot}N{:}C\text{———}N{\cdot}NH_2 \\ \qquad\quad S{\cdot}CHR{\cdot}CO\end{array} \qquad\qquad \begin{array}{l}CO\text{———}N{\cdot}NH_2 \\ S{\cdot}CHR{\cdot}CO\end{array}\quad \text{(II.)}$$

Attempts to prepare the bases (I) by reaction between thiocarbohydrazide, sodium ethoxide and the foregoing esters or ethyl chloroacetate * in alcoholic solution

$$NH_2{\cdot}N{:}C(SNa){\cdot}NH{\cdot}NH_2 + CHRBr{\cdot}CO_2Et = (I) + NaBr + EtOH$$

* By the interaction of thiocarbohydrazide, ethyl chloroacetate and potassium hydroxide Guha and De (*J. Ind. Chem. Soc.*, 1925, 1, 141) obtained a substance quite different from that obtained by us.

did not give pure products; these, however, on treatment with benzaldehyde gave the pure dibenzylidene derivatives

$$CHPh{:}N{\cdot}N{:}\underset{S\cdot CHR\cdot CO}{C\text{———}N}{\cdot}N{:}CHPh$$

3-*Amino*-2 : 4-*diketo*-5-*methyltetrahydrothiazole*-2-*hydrazone* was obtained in the pure condition.

Further experiments were undertaken, but without success, to synthesise compounds containing a thiazole ring fused to another ring structure, two examples of which were given in Part I. *o*-Phenylenethiocarbamide in alcoholic solution in presence of sodium ethoxide reacted with ethyl α-bromopropionate and ethyl α-bromo-*n*-butyrate to give *ethyl benziminazolyl-2-α-thiolpropionate* and *ethyl benziminazolyl-2-α-thiol-*n*-butyrate*, respectively (III; R = Me and Et). Ring closure of these compounds in benzene solution by means of sodium wire or powder could not, however, be effected. *Benziminazolyl-2-α-thiolpropionic acid* and *benziminazolyl-2-α-thiol-*n*-butyric acid* have been prepared. *o*-Phenylenethiocarbamide and chloroacetic acid in boiling aqueous solution gave *benziminazole-2-thioglycollic acid* (formula as III; R = H).

$$\text{(III.)}\quad C_6H_4{<}{}^{NH}_{N}{>}C{\cdot}S{\cdot}CHR{\cdot}CO_2Et \qquad CH_2{<}{}^{CH_2\cdot NH}_{CH_2-N}{>}C{\cdot}S{\cdot}CH_2{\cdot}CO_2Et \quad \text{(IV.)}$$

Methylenethiocarbamide failed to react with ethyl chloroacetate in presence of sodium ethoxide or pyridine. Trimethylenethiocarbamide reacted with ethyl chloroacetate in hot pyridine solution, giving *ethyl* 1 : 4 : 5 : 6-*tetrahydropyrimidine-2-thioglycollate* (IV); this decomposed on heating and was insoluble in benzene, the usual method of effecting ring closure thus being precluded. *o*-Benzoylenethiocarbamide (V) reacted with ethyl chloroacetate in alcoholic solution in presence of sodium ethoxide to give an oil which appeared to be a complex mixture; fractional distillation in a high vacuum failed to effect a separation, but from one of the fractions a small quantity of *ethyl* 4-*keto*-3 : 4-*dihydroquinazoline*-2-*thioglycollate* (VI)

$$\text{(V.)}\quad C_6H_4{<}{}^{CO-NH}_{NH\cdot CS} \qquad C_6H_4{<}{}^{CO\cdot NH}_{N=C\cdot S\cdot CH_2\cdot CO_2Et} \quad \text{(VI.)}$$

was obtained.

Frerichs and Förster (*Annalen*, 1909, **371**, 257) and Frerichs and Höller (*ibid.*, 1913, **398**, 256) found that hydrazodithiodicarbonamide and chloroacetic acid gave in aqueous solution a compound which they regarded as 3 : 3-bis-ψ-thiohydantoin:

$$NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2 + 2CH_2Cl{\cdot}CO_2H =$$
$$NH{:}\underset{S\cdot CH_2\cdot CO\ \ CO\cdot CH_2\cdot S}{C\text{——}N\text{——}N\text{——}C}{:}NH + 2H_2O + 2HCl.$$

We obtained the same compound by heating hydrazodithiodicarbonamide with ethyl chloroacetate in alcoholic solution in presence of sodium ethoxide. As noted by these authors, this compound, although insoluble in all the usual solvents, dissolved in sodium hydroxide solution and was precipitated on acidification; we found in addition that if the alkaline solution was boiled for a short time and then acidified, no precipitate formed, the solution containing thioglycollic acid as shown by Andreasch's test, rupture of the ring having occurred; this test proves the presence of the group C·S·C. Boiling with concentrated hydrochloric acid gradually dissolved the substance, hydrolysis occurring, the products being hydrazine hydrochloride and 2 : 4-diketotetrahydrothiazole. For this reason we ascribe to the compound the structure (VII) of 2 : 4-diketotetrahydrothiazole-2-ketazine in preference to that given by Frerichs, the hydrolysis taking place thus :

$$\text{(VII.)}\quad \begin{array}{l}NH\text{——}C{:}N{\cdot}N{:}C\text{——}NH\\ CO{\cdot}CH_2{\cdot}S\qquad S{\cdot}CH_2{\cdot}CO\end{array} + H_2O = 2\begin{array}{l}NH\text{——}CO\\ CO{\cdot}CH_2{\cdot}S\end{array} + N_2H_4 :$$

it is difficult to see how a compound of the alternative structure could undergo hydrolysis in this manner. The formation of the substance would then be represented thus :

$$NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2 \longrightarrow$$
$$NH_2{\cdot}C(SNa){:}N{\cdot}N{:}C(SNa){\cdot}NH_2 \xrightarrow[(+2CH_2Cl{\cdot}CO_2Et)]{} \text{(VII.)}$$

Hydrazothiodicarbonamide, $NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, did not dissolve in alcoholic sodium ethoxide or pyridine. When it was boiled in aqueous solution with chloroacetic acid, a white precipitate, insoluble in solvents, soon appeared. This was 2 : *4-diketotetrahydrothiazole-2-semicarbazone*, formed thus :

$$NH_2{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2 \longrightarrow NH_2{\cdot}C(SH){:}N{\cdot}NH{\cdot}CO{\cdot}NH_2$$
$$\xrightarrow[(+CH_2Cl{\cdot}CO_2H)]{} \begin{array}{l}NH\text{——}C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2\\ CO{\cdot}CH_2{\cdot}S\end{array} + HCl + H_2O.$$

The yield was rather poor, and the mother-liquor contained 2 : 4-diketotetrahydrothiazole and semicarbazide hydrochloride, evidently produced by hydrolysis of a portion of the substance. Boiling with sodium hydroxide solution gave thioglycollic acid, showing the presence of the group C·S·C. The structure of the compound was proved by boiling with dilute hydrochloric acid, which effected hydrolysis into 2 : 4-diketotetrahydrothiazole and semicarbazide hydrochloride.

In continuation of investigations on the thermal decomposition of carbohydrazones (*J.*, 1927, 107), the decomposition of some thiocarbohydrazones, thiosemicarbazones, and δ-phenylthiosemi-

carbazones on heating was studied, but without very definite results. Diacetophenonethiocarbohydrazone and bis-dibenzyl ketone thiocarbohydrazone were unaffected by prolonged boiling in alcoholic solution; at their melting points they gave ketazines as the only recognisable products. Acetone- and acetophenone-thiosemicarbazones and δ-phenylthiosemicarbazones when heated at or above their melting points yielded the ketazines as the only recognisable products together with ammonia or aniline and hydrogen sulphide.

EXPERIMENTAL.

Reactions with Diacetophenonethiocarbohydrazone.—A suspension of this substance in alcohol containing sodium ethoxide (1 mol.) was boiled for 10 minutes, ethyl α-bromopropionate (slightly more than 1 mol.) was then added, and the boiling continued for ½ hour. The liquid was filtered hot from sodium bromide and on cooling deposited *3-phenylmethylmethyleneamino-2 : 4-diketo-5-methyltetrahydrothiazole-2-phenylmethylmethylenehydrazone*, which crystallised from alcohol in prismatic needles, m. p. 150°; yield, 90% (Found: N, 15·5; S, 8·7. $C_{20}H_{20}ON_4S$ requires N, 15·4; S, 8·8%). *3-Phenylmethylmethyleneamino-2 : 4-diketo-5-ethyltetrahydrothiazole-2-phenylmethylmethylenehydrazone* (needles from alcohol, m. p. 110°) was prepared in the same way from ethyl α-bromo-*n*-butyrate; yield, 90% (Found: N, 15·0; S, 8·4. $C_{21}H_{22}ON_4S$ requires N, 14·8; S, 8·5%). *3-Phenylmethylmethyleneamino-2 : 4-diketo-5-phenyltetrahydrothiazole-2-phenylmethylmethylenehydrazone*, prepared in the same way from ethyl phenylbromoacetate, crystallised from alcohol in prismatic needles, m. p. 165°; yield, 80% (Found: N, 13·2; S, 7·4. $C_{25}H_{22}ON_4S$ requires N, 13·1; S, 7·4%). The three compounds are soluble in alcohol, ether, benzene and chloroform, and insoluble in light petroleum.

In a similar way there was produced from thiocarbohydrazide and ethyl chloroacetate a white solid, which was very soluble in alcohol, pyridine, and water and insoluble in other organic solvents and crystallised from alcohol in prismatic needles, m. p. 119—120°. It was apparently impure *3-amino-2 : 4-diketotetrahydrothiazole-2-hydrazone* (I; R = H) (Found: N, 39·5; S, 23·1. $C_3H_6ON_4S$ requires N, 38·4; S, 21·9%), but repeated crystallisation with change of solvent failed to improve the analytical values. This substance gave a dibenzylidene derivative (m. p. 138°) identical with that previously prepared from the dihydrochloride (Part I, *loc. cit.*). *3-Amino-2 : 4-diketo-5-methyltetrahydrothiazole-2-hydrazone* (I; R = Me) was prepared in a similar manner from ethyl α-bromopropionate with addition of a little dry benzene; after removal of sodium bromide in the heat and of a little unaltered thiocarbo-

hydrazide which separated on cooling, the solution was concentrated *in an evacuated desiccator*. The solid obtained crystallised from alcohol–light petroleum in rhombic plates, m. p. 100—101°, soluble in water and alcohol, insoluble in light petroleum; the yield was small (Found: S, 20·0. $C_4H_8ON_4S$ requires S, 20·0%). The *dibenzylidene* derivative (small prisms from aqueous alcohol, m. p. 114°) was prepared by heating the base with benzaldehyde in alcoholic solution (Found: N, 16·7. $C_{18}H_{16}ON_4S$ requires N, 16·7%). *3-Amino-2 : 4-diketo-5-ethyltetrahydrothiazole-2-hydrazone* was obtained in poor yield by the preceding method from ethyl α-bromo-*n*-butyrate, crystallised from alcohol–light petroleum in glistening plates, m. p. 92—93°, and could not be obtained pure (Found: S, 16·1. $C_5H_{10}ON_4S$ requires S, 18·4%). It is very soluble in water and alcohol and insoluble in light petroleum. The *dibenzylidene* derivative forms prismatic needles, m. p. 106°, from alcohol (Found: N, 16·0. $C_{19}H_{18}ON_4S$ requires N, 16·0%).

Reactions with o-*Phenylenethiocarbamide*.—An absolute-alcoholic solution was boiled with sodium ethoxide (1 mol.) for 10 minutes, ethyl α-bromopropionate (1 mol.) was then added, and the boiling continued for ½ hour. The solution after removal of sodium bromide was concentrated considerably and then made turbid by addition of water. The *ethyl benziminazolyl-2-α-thiolpropionate* (III; R = Me) which separated on standing crystallised from ether–light petroleum in prismatic plates, very soluble in ether, alcohol, and chloroform and insoluble in water and light petroleum. Like the corresponding 2-thioglycollate (Part I), this substance appeared to exhibit dimorphism; the stable variety melted at 100° (yield, 90%) (Found: N, 11·3; S, 12·8. $C_{12}H_{14}O_2N_2S$ requires N, 11·2; S, 12·8%). No blackening was produced on long heating and standing with alkaline lead acetate solution, the absence of the group C:S being thus indicated. Hydrolysis with concentrated hydrochloric acid appeared to give impure benziminazolyl-2-α-thiolpropionic acid, which was subsequently obtained pure by another reaction (p. 1420). *Ethyl benziminazolyl-2-α-thiol-*n*-butyrate* (III; R = Et), prepared in the same way from ethyl α-bromo-*n*-butyrate, showed a similar solubility and also appeared to exhibit dimorphism; the stable variety (long, prismatic needles from ether–light petroleum) melted at 108—109° (yield, 90%) (Found: N, 10·6; S, 12·3. $C_{13}H_{16}O_2N_2S$ requires N, 10·6; S, 12·1%). Hydrolysis with concentrated hydrochloric acid gave *benziminazolyl-2-α-thiol-*n*-butyric acid* [glistening plates from water, m. p. 176° (decomp.)], which had an acid reaction and was soluble in alcohol and insoluble in benzene and chloroform (Found: N, 11·9; S, 13·7. $C_{11}H_{12}O_2N_2S$ requires N, 11·9; S, 13·6%).

Ring closure was attempted with both esters. With the thiol-

propionate sodium wire appeared to give promising results. The ester was heated in dry benzene solution with an excess of the metal; gas was slowly evolved and a yellowish solid appeared, which was occasionally detached from the surface of the metal. After 1½ hours' heating, the benzene, which contained very little dissolved matter, was decanted, and the solid was dried in a desiccator and, after a mechanical removal of most of the sodium, dissolved in absolute alcohol. The warm solution was neutralised with a few drops of concentrated hydrochloric acid and, after removal of sodium chloride, concentrated in an evacuated desiccator. The solid obtained crystallised from absolute alcohol–light petroleum, melted at 179° (decomp.), and was *benziminazolyl-2-α-thiolpropionic acid* (Found: N, 12·5; S, 14·5. $C_{10}H_{10}O_2N_2S$ requires N, 12·6; S, 14·4%).

Since it was thought that this acid had been formed by hydration of a dicyclic structure, the above procedure was modified by neutralising the alcoholic solution with dry gaseous hydrogen chloride instead of the aqueous acid; this was attended, even on ice-cooling, with the production of a very disagreeable odour resembling that of mercaptan. After removal of sodium chloride and concentration in a desiccator a yellow gum remained, a hot acetone solution of which deposited, on cooling, a white, amorphous powder, m. p. 118—119° (Found: N, 10·3%); this was very soluble in water and the solution had an acid reaction. The substance was not the dicyclic compound and was not identified. The experiment was repeated with the thiol-*n*-butyrate; this gave an amorphous powder (from acetone; m. p. 120°) acidic in reaction (Found: N, 9·7; S, 10·2%), which was not the dicyclic compound.

Benziminazole-2-thioglycollic acid was obtained by boiling under reflux for 3 hours *o*-phenylenethiocarbamide and chloroacetic acid (1 mol.) in aqueous solution. The crystals deposited on cooling melted indefinitely. The first crop obtained by recrystallisation from water consisted of needles, m. p. 215°, of the acid; subsequent crops still melted over a range of temperature (Found: N, 13·5. $C_9H_8O_2N_2S$ requires N, 13·5%).

Reaction with Trimethylenethiocarbamide (Schacht, *Arch. Pharm.*, 1897, **235**, 461).—This substance did not react with ethyl chloroacetate in alcoholic solution containing sodium ethoxide; it reacted, however, with this ester (1 mol.) in boiling pyridine solution. After ½ hour's boiling, the dark solution on cooling deposited a brownish solid which crystallised from absolute alcohol in small needles consisting of *ethyl* 1 : 4 : 5 : *6-tetrahydropyrimidine-2-thioglycollate* (IV) (Found: N, 13·8; S, 15·8. $C_8H_{14}O_2N_2S$ requires N, 13·9; S, 15·8%). It was insoluble in the usual solvents except water and alcohol and

melted at 256°, decomposing from 200° upwards. Boiling with sodium hydroxide gave thioglycollic acid, which was detected in the usual way.

Reaction with Benzoylenethiocarbamide (Rupe, *Ber.*, 1897, **30**, 1089).—To a boiling absolute-alcoholic solutiou of the substance, sodium ethoxide (1 mol.) in alcohol was added, and after 10 minutes ethyl chloroacetate (1 mol.). After boiling for ½ hour, the solution was filtered from sodium chloride and evaporated in a vacuum; a mobile oil remained. This was fractionally distilled under very low pressure, but the temperature rose throughout without any indication that a true fractionation was being effected, and analyses of various fractions gave no definite information. Air was bubbled for a short time through one of the higher-boiling fractions: a small quantity of solid consisting of *ethyl* 4-*keto*-3 : 4-*dihydroquinazoline*-2-*thioglycollate* (VI) (fine needles from absolute alcohol, m. p. 149°) was deposited (Found: S, 12·1. $C_{12}H_{12}O_3N_2S$ requires S, 12·1%). A benzene solution of the oil, on being heated with sodium wire, slowly evolved gas with formation of tar.

Reaction with Hydrazodithiodicarbonamide (Freund and Wischewiansky, *Ber.*, 1893, **26**, 2877).—To a hot absolute-alcoholic solution, sodium ethoxide (2 mols.) in alcohol was added, and after 10 minutes ethyl chloroacetate (rather more than 2 mols.). After ½ hour's heating, the bulky white precipitate was collected and, being insoluble in solvents, was washed with water (Found: N, 24·1; S, 27·6. $C_6H_6O_2N_4S_2$ requires N, 24·3; S, 27·8%). The yield was theoretical. This substance, identical with that obtained by Frerichs (*loc. cit.*), decomposed at a high temperature without melting and is regarded by us as 2 : 4-diketotetrahydrothiazole-2-ketazine (VII). It gradually dissolved in boiling concentrated hydrochloric acid, and evaporation then gave a solid, from which hot chloroform extracted 2 : 4-diketotetrahydrothiazole, which was identified by comparison with an authentic specimen; the residue was hydrazine hydrochloride, which was identified by conversion into benzylideneazine. The compound prepared by Frerichs gave the same products when boiled with concentrated hydrochloric acid.

Reaction with Hydrazothiodicarbonamide (Freund and Schander, *Ber.*, 1896, **29**, 2508).—This substance was boiled for a few minutes in aqueous solution with chloroacetic acid (1 mol.); a crystalline precipitate rapidly formed and was filtered off when cold. This was 2 : 4-*diketotetrahydrothiazole*-2-*semicarbazone* and was insoluble in organic solvents and only sparingly soluble in hot water, from which it separated in small, glistening plates, m. p. 221—222° (complete decomp.) after becoming brown at 210° (yield, 35%) (Found: N, 32·0; S, 18·5. $C_4H_6O_2N_4S$ requires N, 32·2; S, 18·4%). Hydro-

lysis with sodium hydroxide gave thioglycollic acid, which was recognised in the usual way. The substance was boiled with dilute hydrochloric acid, and the residue obtained on evaporation was extracted with hot chloroform, which dissolved 2 : 4-diketotetrahydrothiazole, leaving semicarbazide hydrochloride.

Acetophenone-δ-phenylthiosemicarbazone, CPhMe:N·NH·CS·NHPh (fine, pale yellow, prismatic needles from alcohol–benzene, m. p. 195°) was prepared by boiling the two components in alcoholic solution for ½ hour and was deposited in 95% yield on cooling (Found: N, 15·6; S, 11·9. $C_{15}H_{15}N_3S$ requires N, 15·6; S, 11·9%).

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THE ROYAL TECHNICAL COLLEGE,
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CLXXXVI.—*The Mechanism of the Degradation of Fatty Acids by Mould Fungi. Part II.*

By PHILIP DALTON COPPOCK, VIRA SUBRAMANIAM, and THOMAS KENNEDY WALKER.

THE importance of data obtained from experiments with mild oxidising agents at normal temperatures *in vitro*, as a basis upon which to conduct physiological studies of fatty acid catabolism, has been stressed by Dakin (*J. Biol. Chem.*, 1908, **4**, 227), who developed the use of hydrogen peroxide for such purposes. Two of the present authors recently indicated (this vol., p. 803) the possibilities of the use of mould fungi in investigations of this nature, and the inquiry has now been extended to a study of the degradations of *n*-butyric, *n*-valeric and *iso*valeric acids by *Aspergillus niger*.

Although numerous investigations have been carried out from the standpoint of Knoop's hypothesis of β-oxidation, the precise mechanism of such oxidation of lower normal saturated fatty acids in the body is not yet known with certainty, previous experimental work indicating that the first product may be either a β-keto-acid, or a β-hydroxy-acid or an αβ-unsaturated acid. According to Dakin (*J. Biol. Chem.*, 1923, **56**, 43), all of these are equally easily oxidised by the liver and, moreover, are readily interconvertible, hence the uncertainty attaching to the question. We find that

when calcium *n*-butyrate is submitted under appropriate conditions *to the attack of the mould, acetone is produced*, and, according to our experimental evidence, the sequence of changes by which it arises is :

butyric acid ⟶ β-hydroxybutyric acid ⟶ acetoacetic acid ⟶ acetone.

Experiments are now being undertaken to ascertain the behaviour of the mould towards β-hydroxybutyric acid. Crotonic acid was not detected in the calcium butyrate culture media, neither could the mould be induced to grow upon various media containing salts of crotonic acid as sole sources of carbon.

Dakin's *experiments on the oxidation of n*-butyric *acid* with hydrogen peroxide (*J. Biol. Chem.*, 1908, **4**, 77) having shown that attack by this reagent commences initially in two directions, namely, at the β-carbon atom and, to some extent, at the α-carbon atom, search was made in the culture media for possible products of the α-oxidation of the acid, but without success.

On a medium containing calcium *n*-valerate as sole carbon supply, *Aspergillus niger* made satisfactory growth and ultimately a mixture of β-hydroxy-*n*-valeric acid and methyl ethyl ketone was obtained in good yield, but further work will be necessary to determine definitely which of these is the first product.

The *study of the action of the mould on iso*valeric *acid* was of special interest in view of the fact that the work of Embden, of Baer and Blum, and of Friedmann (compare Dakin, "Oxidations and Reductions in the Animal Body," 1922) indicates that in the body this acid suffers both β-oxidation and loss of one methyl group with ultimate production of acetoacetic acid and hence acetone, whereas R. Meyer (*Annalen*, 1883, **219**, 240) found that on oxidation *in vitro* with alkaline permanganate acetone was produced by oxidation at the tertiary hydrogen atom and subsequent splitting off of the *iso*propyl group. The source of the acetone is therefore different in the two cases. Our experiments on the *fermentation of iso*valeric *acid have shown that it is degraded in* accordance with the results of the physiological studies just mentioned, for the following facts were observed and, in our view, are capable of no other plausible explanation. On the sixth day after inoculation, a culture on calcium *iso*valerate gave rise to a small quantity of a substance which gave the iodoform reaction, and another sample of the liquid gave acetone on oxidation. On the tenth day, a sample on treatment with benzenediazonium chloride and sodium acetate developed a red colour and deposited a minute amount of a reddish-brown compound, an indication of the presence

of traces of a substance possessing a reactive methylene or methine group. This was followed on the sixteenth day by the occurrence of acetone in the fermenting medium. Precisely similar behaviour towards the diazonium salt was exhibited by the cultures of *A. niger* on calcium *n*-butyrate media just prior to the appearance therein of acetone, the reactive intermediate, presumably acetoacetic acid in both cases, having apparently but a transitory existence.

Processes for the production of acetone by the action of certain bacteria on starch or on sugars have been known for some years, and recently Challenger and two of the present authors (J., 1927, 200) were able to show that it can also arise by the action of *A. niger* on citric acid. Its formation from butyric acid by mycological agency has not been demonstrated previously, however, neither has the production of methyl ethyl ketone by any fermentative organism been described.

EXPERIMENTAL.

The *A. niger* strain and the medium (solution M) containing the necessary inorganic salts were identical with those employed in the work described in Part I (this vol., p. 803). Incubation of the inoculated media was carried out at 32° unless otherwise stated.

Fermentation of Calcium n-*Butyrate. Detection of* (a) β-*Hydroxybutyric Acid,* (b) *Acetoacetic Acid, and* (c) *Acetone.*—A solution of 25 g. of pure *n*-butyric acid (as calcium salt) in 2500 c.c. of solution M was sterilised at 100° for 15 minutes on three successive days. After inoculation with spores of the mould the solution was incubated and portions were withdrawn daily for submission to the following tests:

(i) 10 C.c. for the iodoform test, which, if positive, would indicate the presence of (*a*), (*b*) or (*c*).

(ii) 20 C.c. were treated with benzenediazonium chloride and sodium acetate to detect the appearance of (*b*).

(iii) 100 C.c. were distilled and two successive fractions were collected. The first fraction (30 c.c.) was heated with 500 c.c. of Denigès' mercuric sulphate solution under reflux on a steam-bath (compare J., 1927, 206) to detect acetone and/or acetoacetic acid. The second fraction (10 c.c.) was tested similarly in order to ensure, in the event of acetone being found in the first fraction, that the residue in the distillation flask (60 c.c.) should be quite free from acetone. A mixture of this residue (60 c.c.) with 20 c.c. of 50% sulphuric acid was then gently boiled and 30 c.c. of 2% potassium dichromate solution were added slowly while distillation proceeded. The distillate (30 c.c.) was heated with Denigès' solution (500 c.c.) as before. This served to detect the presence of any β-hydroxybutyric acid. By the adoption of this plan the sequence in which

the products of oxidation made their appearance in the fermenting culture was readily determined.

On the sixth day after inoculation, test (i) was positive and test (iii) indicated the presence of β-hydroxybutyric acid. On the eighth day, test (ii) gave a red solution containing particles of solid matter, but in an insufficient amount to justify an attempt to convert into a formazyl derivative any acetoacetic acid which might be present. A confirmation of the latter reaction was afforded by the fact that another portion of the culture, removed simultaneously and treated with neutral ferric chloride solution, developed a faint purple colour (a reaction of acetoacetic acid). This was followed on the eleventh day by a slight evolution of carbon dioxide and a positive test for acetone in the culture liquid. The whole of the latter was thereupon distilled, the distillate boiled with Denigès' solution, and the resultant copious precipitate washed with water, drained on a tile, and distilled, in portions, with sodium iodide solution. When treated in the appropriate manner with benzaldehyde, caustic soda, and ethyl alcohol, the united distillates readily gave dibenzylideneacetone, m. p. 113° alone or mixed with authentic material (Found : C, 87·0; H, 6·0. Calc. : C, 87·2; H, 6·0%).

The quantity of β-hydroxybutyric acid present at any one time in the fermenting medium, prior to the appearance of acetone, was very small as judged from the quantities of precipitate obtained when the oxidised culture samples were boiled with Denigès' reagent. In this case also the mercury compound was distilled with sodium iodide solution and the resulting acetone was characterised as dibenzylideneacetone, m. p. and mixed m. p. 113°.

In subsequent fermentation experiments with calcium *n*-butyrate it was found that the yields of acetone varied greatly (5% to 60%). Further experiments are in progress with other salts of butyric acid in order to discover the optimum conditions for production of the ketone.

Fermentation of Calcium n-*Valerate.—Isolation of methyl ethyl ketone.* 2000 C.c. of solution M to which 20 g. of *n*-valeric acid (as calcium salt) had been added were sterilised as in the case of calcium butyrate, inoculated, and incubated at 32°. Growth was slow and products of enzymic action could not be detected in the medium during the first 21 days; vegetative growth then appeared to cease. After remaining at 20° for a further 14 days, a test portion having given an immediate precipitate on treatment with a solution of *p*-nitrophenylhydrazine acetate, the culture liquid was submitted to three careful fractional distillations through a 12-pear Young column. The final distillate was turbid, and clarified on the

separation of an oil; this was identified as methyl ethyl ketone (yield, *ca.* 50%) by conversion into the semicarbazone, m. p. 143°, and into the *p*-nitrophenylhydrazone (Found: C, 57·7; H, 6·4. Calc.: C, 58·0; H, 6·3%), m. p. 128°, each of which did not depress the m. p. of authentic material.

Detection of β-*hydroxyvaleric acid.* The residue in the distillation flask, from which the methyl ethyl ketone had been removed as described above, was oxidised by means of the usual mixture of sulphuric acid and sodium dichromate, and submitted to distillation; a further considerable quantity of methyl ethyl ketone (identified in the forms of the *p*-nitrophenylhydrazone and the semicarbazone) was then obtained. A control experiment in which several grams of pure *n*-valeric acid were distilled in the presence of a considerable quantity of a similar oxidising mixture gave no trace of methyl ethyl ketone.

Fermentation of Calcium iso*Valerate. Detection of Acetone and of its Precursors.*—The medium used consisted of solution M (2500 c.c.) to which had been added 25 g. of calcium *iso*valerate (Kahlbaum), and the whole was sterilised and inoculated as before. During incubation daily tests were performed as in the case of the calcium butyrate cultures. After 6 days, the distillate from an oxidised test portion, on being heated under reflux on the steam-bath with excess of Denigès' reagent, gave a white precipitate (A). After 10 days, a red coloration and a slight precipitate were produced on addition of benzenediazonium chloride and sodium acetate, and this behaviour continued until the sixteenth day; acetone, in small quantity, was then first detected in the culture. In this particular experiment the yields of all three products were very small, but in a subsequent fermentation 25 g. of calcium *iso*valerate, after 14 days' undisturbed incubation, gave 3·5 g. of acetone, calculated on the weight of Denigès' mercury compound (B) obtained from it. Both lots (A and B) of mercury compound were decomposed separately by treatment with sodium iodide solution, and the liberated acetone was characterised in each case as dibenzylideneacetone (m. p. 113°) and as the *p*-nitrophenylhydrazone (m. p. 148·5°). In no case did the mixed m. p. determination show depression. The dibenzylidene compound derived from (A) was analysed (Found: C, 86·9; H, 6·1. Calc.: C, 87·2; H, 6·0%). Blank experiments showed that pure *iso*valeric acid gives no acetone on being heated with a sodium dichromate and sulphuric acid mixture of the concentration used in this work.

(*Note added, May 16th, 1928*).—Since this paper was prepared for publication W. N. Stokoe (*Biochem. J.*, 1928, 22, 80) has made known the results of an investigation of the action of moulds,

principally of the *Penicillium* genus, on coco-nut oil. Our attention has also been directed to the observations of H. G. Derx (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 96) on the oxidative cleavage of fats by fungi and, further, we have noted the very recent work of W. O. Tausson (*Biochem. Z.*, 1928, **193**, 85) on the oxidation of waxes by micro-organisms. By the employment of experimental conditions somewhat different from those adopted by us, in that we fermented salts of the fatty acids in the entire absence of any other sources of carbon, Stokoe and Derx obtained methyl ketones from several fatty acids which are higher in the series than valeric acid and are normally present in the glycerides of coco-nut oil. Derx did not observe ketone formation, however, when butyric and valeric acids were submitted to the action of cultures of a *Penicillium* species in a glucose medium. In general principle, the experimental results recorded in these papers are in substantial agreement with those obtained by us, inasmuch as they all demonstrate clearly the origin of the methyl ketones found in certain plant products (compare Dakin, *J. Biol. Chem.*, 1908, **4**, 221). In the interpretation of the precise course of the oxidation in the case of a straight-chain acid we differ from Stokoe and Derx, who presume that a β-keto-acid is the first product, whereas our evidence points to the initial formation of a β-hydroxy-acid and its subsequent oxidation to the corresponding β-keto-acid.

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CLXXXVII.—*Organic Derivatives of Silicon. Part XXXVI. Highly Complex Condensation Products of Diphenyl- and Di-p-tolyl-silicanediol. Fission of the Si–Ph Link.*

By FREDERIC STANLEY KIPPING and ARTHUR GEORGE MURRAY.

THREE open-chain and two closed-chain condensation products of diphenylsilicanediol have been described (Kipping, J., 1912, **101**, 2108; Kipping and Robison, J., 1914, **105**, 484); all these compounds crystallise well and their molecular weights have been determined cryoscopically.

By the action of hot alkalis on diphenylsilicanediol two much

more complex substances have been obtained : the one, $(SiPh_2O)_A$, is practically insoluble in all ordinary solvents, whereas the other, $(SiPh_2O)_B$, is appreciably but only sparingly soluble in boiling benzene, and both seem to be amorphous. The compound $(SiPh_2O)_B$ gives in camphor $M = 3900$, corresponding with $B = 19$ or 20; judging from its insolubility, the other product is even more complex.

The known condensation products of di-*p*-tolylsilicanediol are the open- and the closed-chain compounds formed from three molecules of the diol, and a substance (m. p. 186—187°) which is probably $[Si(C_7H_7)_2O]_4$ (Pink and Kipping, J., 1923, **123**, 2833). Two new substances, which seem to correspond respectively with the two diphenyl analogues described above, have been obtained. The product insoluble in benzene, $[Si(C_7H_7)_2O]_A$, gives in camphor $M = 3450$, but the results are not trustworthy owing to the slight solubility of the substance; the more soluble compound gives $M = 4150$, a value which is probably approximately correct.

If the actual molecular weights are of the indicated order of magnitude, as seems very probable, the open-chain compound $HO{\cdot}SiR_2(O{\cdot}SiR_2)_n{\cdot}O{\cdot}SiR_2{\cdot}OH$ would have practically the same composition as the closed-chain compound; so that although the results of silicon determinations agree very closely in all cases with those required for SiR_2O, one or more of the products may have the open-chain structure; it is also possible that one or more of the products may be a mixture.

In any case the compounds are not without theoretical interest : if they consist of closed chains of some 20 $-SiR_2O-$ groups, their existence would emphasise the conclusions which may be drawn from the results of Ruzicka's work on the cyclic ketones; if, on the other hand, they are open-chain compounds, it would seem that the silicanediols, like methylene glycol, may give rise to a very extended series of condensation products.

In the course of the above experiments and in many previous investigations in which diphenylsilicanediol, its condensation products, and other compounds containing the $-SiPh_2-$ group were heated with alkalis, the formation of benzene was never observed. Recently, however, it has been found that certain dibenzylsilicon derivatives are decomposed by sodium hydroxide solution with fission of the carbon–silicon binding and it seemed possible that diphenyl analogues might behave in a similar manner.

Experiments then showed that diphenylsilicanediol is slowly decomposed by 20% potassium hydroxide solution at 95—100°, with evolution of benzene, and it is therefore almost certain that a portion of the diol is decomposed in this way during the formation of the above-described condensation products. The results of the silicon

determinations seem, however, to prove conclusively that the compounds in question contain two aryl groups for every silicon atom: if even one phenyl group were displaced by hydroxyl in a compound $(SiPh_2O)_{20}$, the percentage of silicon would be raised to 14·5.

EXPERIMENTAL.

The two diphenylsilicanediol derivatives are precipitated, together with smaller quantities of the more soluble condensation products, when diphenylsilicon dichloride (10 g.), dissolved in a little acetone, is gradually added to a 10% aqueous solution of potassium hydroxide (200 c.c.) and the clear liquid is then evaporated on the water-bath to about 75 c.c.; the solution is then practically free from diol. The insoluble products are not formed if the original solution is merely heated at 100° on a reflux apparatus, as, apparently, a certain concentration of alkali must be reached. For instance, with a 2½% solution of alkali under the conditions stated, an oily product, probably dianhydrotrisdiphenylsilicanediol, is obtained, whereas with a 5% solution, crystalline products (trianhydrotris- and tetra-anhydrotetrakis-diphenylsilicanediol) are formed and these are only very slowly converted into the more complex substances by further evaporation at 100°. The insoluble products are also formed when a 5% solution of potassium hydroxide is added rapidly to diphenylsilicon dichloride.

The precipitate is repeatedly washed with water and then extracted in a Soxhlet apparatus with acetone during 6—8 hours to remove the lower condensation products. The extraction is then continued with boiling benzene during 2—3 days and the residue (A) is finally extracted with boiling water. The benzene extracts when cooled deposit a gelatinous product (B), which is separated by filtration: the mother-liquors contain traces of the crystalline condensation products.

The insoluble residue (A) is colourless and does not melt at 360°, but decomposes at much higher temperatures; it seems to be amorphous (Found: Si, 14·2, 14·2, 14·1. $SiPh_2O$ requires Si, 14·3%). It is practically insoluble in all the ordinary solvents and is only very sparingly soluble in melted camphor, but it dissolves freely in boiling aniline; from this solvent it separates again when the solution is cooled as an amorphous powder even after the solution has been boiled during 2 hours, but in presence of a little water it undergoes hydrolysis and in the course of 4 hours is completely decomposed, giving trianhydrotrisdiphenylsilicanediol and other soluble condensation products, together apparently with a little of the substance (B). Its behaviour towards phenol is much the same as towards aniline. It is not appreciably changed when

it is boiled with a 5% solution of potassium hydroxide in aqueous acetone during several hours, but when heated with very concentrated *alkali at 150° it is slowly decomposed, giving benzene* and a silicate.

The product (B), which forms only a very small proportion of the original mixture, separates from benzene or chloroform in a gelatinous form, but soon becomes brittle as the solvent evaporates, giving a colourless, apparently amorphous powder (Found: Si, 14·2, 14·2. $SiPh_2O$ requires Si, 14·3%. *M* in camphor 3900, 3710). It is practically insoluble in acetone, alcohol, ether, etc., and is only sparingly soluble in benzene and chloroform. It begins to sinter at about 300° and gradually liquefies at a considerably higher temperature. It is very slowly hydrolysed by an acetone solution of potassium hydroxide, giving a salt of diphenylsilicanediol.

Di-*p*-tolylsilicon dichloride, dissolved in a 10% aqueous solution of potassium hydroxide (25 parts), gives first an oily and finally a solid product when the solution is evaporated on the water-bath, and practically the whole of the diol undergoes condensation. The solid is washed with water and then extracted with boiling acetone, which dissolves a little of the compound, m. p. 186—187° (*loc. cit.*), and some oily matter. When the residue is extracted with boiling benzene, about one half of it, $[Si(C_7H_7)_2O]_B$, dissolves, leaving the product $[Si(C_7H_7)_2O]_A$, which is again extracted with water.

The insoluble substance, $[Si(C_7H_7)_2O]_A$, is a colourless, amorphous powder, not appreciably soluble in the common solvents [Found: Si, 12·5. $Si(C_7H_7)_2O$ requires Si, 12·5%. $M = 3450$]. It shows signs of sintering at 270°, but it is not completely melted at 360°. When it is boiled with a 5% aqueous solution of potassium hydroxide it is not appreciably changed.

The benzene extract (see above), when evaporated or mixed with petroleum, gives a gelatinous solid similar to the corresponding diphenyl compound [Found: Si, 12·4. $Si(C_7H_7)_2O$ requires Si, 12·5%. $M = 4150$]. It sinters at about 260°, but does not melt completely at 360°; it is readily soluble in camphor, benzene, and chloroform, but is practically insoluble in acetone; it is only very slowly hydrolysed by a 5% solution of potassium hydroxide in aqueous acetone.

The fission of the Si–Ph binding was proved by heating diphenylsilicanediol with a 20% aqueous solution of potassium hydroxide on the water-bath under reduced pressure, and collecting the benzene in wash-bottles containing nitric and sulphuric acids. After 3 hours' heating, the quantity of benzene produced, estimated as the dinitro-derivative, was about 1% of the diol used, and the alkaline solution gave at once a heavy precipitate with acids. On prolonged heating,

however, the filtered alkaline solution gave no immediate precipitate when acidified, and the flocculent deposit which gradually formed was insoluble in organic solvents and seemed to consist principally of silica.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, March 24th, 1928.*]

CLXXXVIII.—*Organic Derivatives of Silicon. Part XXXVII. The Production of Tetrabenzylsilicane, Tribenzylsilicyl Oxide, and Other Products by the Action of Sodium on Dibenzylsilicon Dichloride.*

By ALFRED RAYMOND STEELE and FREDERIC STANLEY KIPPING.

THE reactions which occur when dibenzylsilicon dichloride in toluene solution is treated with sodium and potassium in absence of oxygen are very complex and the final results are quite different from those obtained with diphenylsilicon dichloride (Kipping and Sands, J., 1921, **119**, 830, 848; Kipping, J., 1923, **123**, 2590, 2598; 1924, **125**, 2291; 1927, 2719). No silicohydrocarbon corresponding with one or other of the four (A, B, C, D) diphenyl compounds $(SiPh_2)_n$ has been isolated; the soluble product contains a very small proportion of tribenzylsilicyl oxide, $[Si(CH_2Ph)_3]_2O$, and about 15% of tetrabenzylsilicane, the rest consisting of a glue-like or resinous substance.

The formation of the tri- and tetra-benzyl derivatives involves that of a corresponding quantity of material rich in silicon, which is insoluble in toluene and other solvents; this product is variable in composition and seems to be composed of compounds which contain less than one benzyl group for each silicon atom.

The synthesis of the tri- and tetra-benzyl derivatives is doubtless due to the formation of sodium or potassium compounds at some stage of the interaction and it may therefore be suggested that the $>Si(CH_2Ph)_2$ groups of some of the intermediate products give $>Si(CH_2Ph)Na$ and CH_2PhNa; the latter reacting with unchanged dichloride would then yield the tetra- and tri-benzyl derivatives, and the products containing the $>Si(CH_2Ph)Na$ complexes, on treatment with water, would give the material insoluble in toluene and rich in silicon. The great difference between the products from diphenyl- and those from dibenzyl-silicon dichloride would thus be due to the relative instability of the $>Si(CH_2Ph)_2$ complex towards alkali metals.

The resinous product, separated from the tetrabenzylsilicane (and tribenzylsilicyl oxide) by systematic fractionation, is somewhat

similar in outward properties to the non-crystalline substance obtained from diphenylsilicon dichloride (J., 1927, 2719). When alcohol is added to its acetone solution, it is precipitated as an oil which gradually hardens to a resin, but it may be obtained as a highly lustrous flaky solid by frothing its ethereal solution.

A prolonged investigation of this product has given results which seem to prove that it is an octabenzylsilicotetrane oxide, $[Si(CH_2Ph)_2]_4O$, mixed possibly with analogous oxides; since successive fractions are practically identical in composition, it may be concluded with some confidence that they are homogeneous or if not that they consist entirely of very nearly related substances.

The proportion of oxygen in a compound $[Si(CH_2Ph)_2]_4O$ is so small (1·8%) that its estimation by difference might give very untrustworthy results; it seems certain, however, that the fractions do not consist of silicohydrocarbons, because when decomposed with alkalis they all give a hydrogen value (J., 1921, *loc. cit.*) of about 80, corresponding closely with that (79) required for $[Si(CH_2Ph)_2]_4O + 7H_2O = 4Si(CH_2Ph)_2(OH)_2 + 3H_2$ and widely different from that (107) required for $[Si(CH_2Ph)_2]_4$. This result is certainly not due to the presence of tetrabenzylsilicane or tribenzylsilicyl oxide, and it seems most improbable that all the fractions could consist of a mixture of silicohydrocarbons with about 20% of dibenzylsilicanediol or its condensation products, quite apart from the difficulty of accounting for the formation of the diol; the amorphous product must therefore be regarded as the oxide $[Si(CH_2Ph)_2]_4O$.

The source of the combined oxygen in this resinous substance and in the tribenzylsilicyl oxide has not been traced. Dibenzylsilicon dichloride, unlike the diphenyl analogue, is easily obtained free from ethoxy-compounds, and only pure material was used; further, after some preliminary experiments had shown the formation of tribenzylsilicol, the interaction with sodium was carried out in an atmosphere of nitrogen, oxygen and moisture being carefully excluded. Nevertheless, when the original toluene solution, filtered as far as possible in an atmosphere of nitrogen, is rapidly evaporated under reduced pressure and the residue mixed with dry ether, the solution usually gives a precipitate of tribenzylsilicyl oxide. Now the 0·02 g. of oxygen in the oxide thus obtained might originate in traces of moisture in the materials and apparatus and from traces of dibenzylsilicon hydroxychloride,

$$Si(CH_2Ph)_2(OH)Cl,$$

in the dichloride; but the 0·3 g. of oxygen contained in the fractionated product from 50 g. of the dichloride must have some other source. Analytical results seem to prove that the oxygen is taken up before

exposure to the air or to any solvents containing water; moreover, the freshly prepared product (containing tetrabenzylsilicane) seems to be inert towards atmospheric oxygen, even at 100°, and does not combine with iodine to an appreciable extent; presumably, therefore, the oxygen in the fractionated product is not due to the action of the air or of aqueous solvents on some unstable compound containing tervalent silicon analogous to octaphenylsilicotetrane (A).

When the original toluene solution contained in a flask filled with nitrogen is poured on to a dry filter, a vigorous effervescence is often observed not only on the filter but also in the filtrate (collected in nitrogen). This gas evolution, which soon ceases, is apparently due to the admission of moisture, whereby the metallic derivatives in solution or in suspension are decomposed with the formation of alkali hydroxide; the latter then reacts with some unstable silicon compounds, possibly containing $Si(CH_2Ph)_2H$ groups, with liberation of hydrogen and formation of oxides:

$$\begin{matrix}-Si(CH_2Ph)_2H\\-Si(CH_2Ph)_2H\end{matrix} + H_2O = \begin{matrix}-Si(CH_2Ph)_2\\-Si(CH_2Ph)_2\end{matrix}{>}O + 2H_2.$$

The effervescence thus brought about is very transitory, and in most experiments any further action of alkali was inhibited by the addition to the filtrate of a few drops of acetic acid; it is therefore almost impossible to believe that the whole of the oxygen in the product originates in this way, and the only reasonable suggestion seems to be that it is obtained from oxides present in the alkali metals. So large a proportion of these metals is used that even about 3% of oxygen would be sufficient to account for the results. From the whole of the evidence it is inferred that during the earlier stages of the interaction, the dibenzylsilicon dichloride is converted into $Si(CH_2Ph)_2Cl{\cdot}Si(CH_2Ph)_2Cl$ and then into

$$Si(CH_2Ph)_2Cl{\cdot}Si(CH_2Ph)_2{\cdot}Si(CH_2Ph)_2{\cdot}Si(CH_2Ph)_2Cl;$$

the latter, instead of giving the open- and closed-chain compounds corresponding with octaphenylsilicotetrane (A) and octaphenyl*cyclo*silicotetrane (B), is partly decomposed by the alkali metals, giving sodium benzyl and products rich in silicon, the rest reacting with alkali oxides to form octaphenylsilicotetrane oxide: the sodium benzyl with unchanged dichloride gives tetrabenzylsilicane and tribenzylsilicyl chloride, the latter being then transformed into the oxide: $2Si(CH_2Ph)_3Cl + Na_2O = [Si(CH_2Ph)_3]_2O + 2NaCl$.

Some of the evidence on which these views are based is derived from the results of parallel researches now in progress; an account of these will be published later and it is hoped that light may then be thrown on the unsolved problems of this investigation. One interesting question is, Why is the oxide $[Si(CH_2Ph)_2]_4O$ amorphous?

The corresponding phenyl derivative, $(SiPh_2)_4O$, is crystalline and melts above 200°; possibly, therefore, the benzyl compound exists in two forms, analogous respectively to the crystalline and the amorphous variety of octaphenyl*cyclo*silicotetrane.

The many difficulties met with in this work have been enhanced by the unsuspected fact that some benzyl derivatives of silicon are easily attacked by alkalis, with fission of the carbon–silicon binding; dibenzylsilicol, for example, is decomposed into toluene and silica or benzylsiliconic acid at temperatures below 100°.

EXPERIMENTAL.

All the dibenzylsilicon dichloride used in these experiments was very carefully purified, first by distillation,* and then by recrystallisation from light petroleum; it melted at 47—48° † and was completely soluble in a cold aqueous solution of potassium hydroxide, showing its freedom from tri- and tetra-benzyl derivatives. All samples gave 25·0—25·1% of chlorine [$Si(CH_2Ph)_2Cl_2$ requires Cl, 25·2%].

Sodium ($2\frac{1}{4}$ atoms), freshly freed under toluene from superficial oxide, is quickly added to a solution of the dichloride (1 mol.; 50 g.) in dry toluene (500 c.c.) contained in a flask through which dry nitrogen ‡ is immediately passed, and after all the air is expelled, heat is applied. A reaction starts when the toluene nears its boiling point, a dark brown, almost black crust being formed on the globules of sodium; later on, the flask is vigorously shaken from time to time in order to expose fresh surfaces of the metal. After some 20 hours of gentle ebullition a test portion of the filtered yellow solution usually shows the presence of silicon halides, and gives with water an acid reaction and a precipitate with silver nitrate solution. As such halides or the hydroxy-compounds to which they would give rise would have contaminated the product, and as their complete removal with sodium takes a very long time —during which there is a constant danger of a fracture of the flask —potassium (1—2 g.) is now added and the boiling continued during about 5 hours until the decomposition is complete. The toluene solution is then pale yellow, or it may have acquired a mahogany colour; in the former case, it gives a neutral, in the latter a strongly

* The fractions of low boiling point gave ethyl alcohol on hydrolysis and doubtless contained ethoxy-derivatives (compare Kipping and Murray, J., 1927, 2734).

† The melting point (50—52°) given by Martin and Kipping (J., 1909, **95**, 307) seems to be rather too high.

‡ Earlier unpublished experiments carried out by Dr. Robison and one of us having shown that tribenzylsilicol could be isolated from the reaction product, it seemed advisable to exclude oxygen.

alkaline, aqueous extract when a filtered portion is shaken with water, but in either the extract is free from chlorides. When cold, the contents of the flask are quickly transferred to a filter, so enclosed between two desiccator covers that the whole operation can be conducted in a stream of nitrogen. The toluene filtrate, immediately evaporated under reduced pressure, gives a thick yellow or mahogany-coloured oil, described later (p. 1436). In the case of the mahogany-coloured solutions the momentary exposure to the air during their transference to the filter sets up the brisk effervescence referred to on p. 1433.

The Insoluble Product.—The bulky dark brown mass on the filter is well washed with toluene * and is then cautiously added to cooled alcohol containing a permanent excess of acetic acid in order to avoid the decomposition of silicon compounds by alkali. The metals having been transformed into their acetates, water is added to dissolve the dark brown mass of halides; there results a colourless solution containing in suspension a flocculent or granular material, which is separated by filtration, well washed with water, and then extracted with hot acetone to free it from a small proportion of glue-like matter.

This product is a slightly greyish powder, insoluble in all common solvents, including boiling phenol, aniline, etc., and it does not give hydrogen when it is heated with an acetone or alcoholic solution of potassium hydroxide. Different preparations contained 28—34% of silicon [$Si{\cdot}CH_2Ph$ requires Si, 23·5%. $(CH_2Ph{\cdot}SiO)_2O$ requires Si, 19·8%], and when evaporated two or three times with hydrofluoric acid they left from 12 to 17% of a dark carbonaceous residue free from silicon; it was therefore impossible to prove the presence of silica. It is clear, however, that this product bears no relation to the insoluble substance (D) obtained from diphenylsilicon dichloride (*loc. cit.*); possibly it is a mixture of silica and condensation products of benzylsiliconic acid from the action of water on sodium silicide and sodium benzylsilicide, respectively.

The yield of this material is about 1 g. from 50 g. of the dichloride; its total silicon content corresponds roughly with that calculated from the estimated weight of the tetrabenzylsilicane which is produced in the reaction.

Isolation of Tribenzylsilicyl Oxide.—In the first experiments carried out in nitrogen the *yellow* toluene filtrate of the crude product kept in a closed flask deposited crystals of tribenzylsilicyl oxide in the course of some days; as this might have been the result of atmospheric oxidation, in later experiments the solution was

* As air is admitted during this operation, the washings are not added to the original filtrate.

immediately evaporated and the oily residue mixed with dry ether (6—8 vols.), the air in the flask being displaced by nitrogen. The *crystalline* product (about 1 g.) then precipitated was, after recrystallisation, fully identified as tribenzylsilicyl oxide by its melting point (205—206°), analysis {Found: Si, 9·1. Calc. for $[Si(CH_2Ph)_3]_2O$: Si, 9·1%}, direct comparison, and a mixed melting point determination.

The Main Components.—The yellow oil, obtained from the ethereal filtrate, slowly changes to a transparent resinous mass as the last portions of solvent volatilise. This material is miscible with all the common solvents with the exception of alcohols, acetic acid, and light petroleum, in which it is only sparingly soluble. In benzene solution it does not combine with iodine to an appreciable extent and seems, therefore, to be free from compounds containing tervalent silicon. It does not seem to undergo atmospheric oxidation even at 100°, but its glue-like character and the tenacity with which it retains solvent preclude accurate gravimetric or volumetric determinations, and it is possible that some slight oxidation may occur. Its acetone solution reduces silver nitrate in a marked manner, but no definite oxidation product could be isolated. Various preparations, freed from solvent by exposure to reduced pressure during many days, gave 11·9 to 12·2% of silicon, and hydrogen values of 58—60 [$Si(CH_2Ph)_2$ requires Si, 13·4%; H.V., 107]; these results are considered later (p. 1438).

Isolation of tetrabenzylsilicane. The crude product is fractionally precipitated with alcohol from its solution in cold acetone and is thus directly separated into 8—12 portions, each of which is systematically treated in a similar manner many times, but without increasing the number of fractions. The precipitate is an oil in all cases, but, as the oil is mixed with a considerable proportion of solvent, each precipitation gives a very partial separation. After these operations the solutions of the two or three more soluble portions deposit a crystalline compound which, after recrystallisation from chloroform and light petroleum, melts at 128—129° and is further identified as tetrabenzylsilicane by analysis [Found: Si, 7·15. Calc. for $Si(CH_2Ph)_4$: Si, 7·2%].

The quantity of tetrabenzylsilicane which can be isolated is about 4—5 g. from 50 g. of the dichloride, but a little no doubt remains in the neighbouring fractions of the glue-like matter; so far as can be ascertained, the crude soluble product, after removal of the tribenzylsilicyl oxide, contains about 15% of the tetrabenzyl compound.

The principal product. The 8—10 less soluble fractions, from which no further crystalline deposits are obtained by continued

operations, consist of thick oils which gradually harden to transparent or translucent, brittle masses. The least soluble (I) and the next two (II, III) are frothed up (Kipping, J., 1927, 2719), and the resulting scaly products—which look beautifully crystalline to the unaided eye—freed from solvent in a vacuum—an operation lasting many days. Such preparations melt indefinitely over a range of 10° between 40° and 60°, show no sign of crystalline structure under the microscope, and give the following analytical results :

Fraction.	Si %.	C %.	H %.	*M*.	H.V.
I.	13·2	78·3	6·8	857	82
II.	13·3	78·1	6·8	785	79·8
III.	13·3	—	—	734	78·5
$[Si(CH_2Ph)_2]_4$ requires	13·4	80·0	6·6	840	107
$[Si(CH_2Ph)_2]_4O$ requires	13·2	78·5	6·5	856	78
$[Si(CH_2Ph)_2]_3O$ requires	13·1	78·0	6·5	646	69
$Si(CH_2Ph)_2O$ requires	12·5	74·0	6·0	226	—

These data seem to show that the three fractions are practically identical in composition and even the more soluble ones (IV, V) give only slightly lower hydrogen values and contain a slightly larger proportion of oxygen; the fractions I—III, therefore, are in all probability homogeneous, or else composed of mixtures of closely related compounds. Analytical data practically identical with the above were given by fractions from other preparations in which the ethereal solution of the crude *yellow* product was precipitated with alcohol; some of these fractions were systematically extracted with boiling light petroleum or boiling alcohol, but in no case was it possible to obtain the principal component in a crystalline form.

From the above results, especially the hydrogen values, it must be concluded either that the main products are oxides or that, if *they consist principally of silicohydrocarbons* $[Si(CH_2Ph)_2]_n$, *the* latter must be mixed with about 20% of some impurity which does not give hydrogen with alkali. But it can be shown that the preparations do not contain any substance $[Si(CH_2Ph)_2]_n$ analogous to (C) which resists fission, because they can be completely converted into compounds soluble in aqueous alkali (p. 1438); unless, therefore, the impurity in question is dibenzylsilicol or one of its condensation products, the presence of which is not excluded by this fact, the preparations cannot consist of $[Si(CH_2Ph)_2]_n$.

Now it is difficult to believe that a mixture of silicohydrocarbons and dibenzylsilicol (or condensation products thereof) would remain constant in composition after exhaustive fractionation; and to assume that such impurities are present would necessitate the conclusion that a large proportion of the original product $[Si(CH_2Ph)_2]_n$ undergoes fission during its treatment with acetone and alcohol. Further, the original product gives a hydrogen

value (58—60) much lower than that of a mixture of $[Si(CH_2Ph)_2]_n$ with the estimated proportion of tetrabenzylsilicane; if free from oxygen, therefore, it must contain about 50% of $Si(CH_2Ph)_4$, in which case it would give only 10·3% of silicon instead of 11·9—12·2 as actually found (p. 1436).

For these reasons it is concluded that the main product consists of the oxide $[Si(CH_2Ph)_2]_4O$, formed in the manner already suggested.

Products from Mahogany-coloured Solutions.—The rapid darkening of the toluene solutions observed in some cases occurs only towards the end of the experiment; it seems very probable, however, that the soluble sodium compounds, to which the colour is due, may be formed at much earlier stages, but are decomposed again so long as any halogen remains combined with silicon. The residue, obtained by filtering and evaporating the solution in absence of air, mixed with ether, gives a dark, flocculent substance (about 1 g. from 50 g. of the dichloride), the solution losing its colour.

This product was soluble in chloroform, from which it separated as a blood-red resin; treated with acetic acid, it gave a colourless, glue-like mass, from which nothing crystalline was obtained. The ethereal filtrate from the dark precipitate did not give any appreciable quantity of tribenzylsilicyl oxide, but the yellow oil obtained from it, systematically fractionated in the manner described above (p. 1436), gave the usual proportion of tetrabenzylsilicane. Analyses of the less soluble fractions showed that they had hydrogen values considerably lower than the corresponding preparations from the yellow toluene solutions; the data indicated mixtures of $[Si(CH_2Ph)_2]_4O$ and $[Si(CH_2Ph)_2]_4O_2$. It seems, therefore, that when the heating is continued beyond a certain stage some of the oxide $[Si(CH_2Ph)_2]_4O$ is converted into sodium or potassium derivatives from which other oxides are subsequently formed.

Fission of the $\geqslant$Si·CH_2Ph *Linkage.*

During the early stages of this work it seemed that the main product from the dichloride must be a silicohydrocarbon $[Si(CH_2Ph)_2]_n$ and that the low hydrogen values might be due to the presence of some 20% of a compound $[Si(CH_2Ph)_2]_n$ which, like the substance (C) from diphenylsilicon dichloride, was not attacked by alkalis.

Various samples of the fractionated substance were therefore heated with aqueous acetone and alkali until effervescence ceased; the acetone was then evaporated and the aqueous solution of the sodium derivative of the diol filtered from insoluble matter. By one such treatment, only a portion of the material was obtained in a soluble form, because of the formation of condensation products

of the diol; after repeated operations, however, practically the whole was obtained in aqueous alkali solution, the residue (less than 1%, if any) consisting of tribenzylsilicyl oxide. Some of the aqueous alkaline solutions obtained in this way gave with acids a bulky precipitate of dibenzylsilicol; but others did not: the latter, after variable periods, deposited gelatinous matter which was insoluble in organic solvents, but soluble in caustic alkalis; various samples of this product gave 26—36% of silicon [$Si(CH_2Ph)_2O$ requires Si, 12·4%], results which indicate mixtures of silica with condensation products of $CH_2Ph{\cdot}Si(OH)_3$.

Further experiments showed that toluene was formed when the *fractionated resin* was heated *on a water-bath during about ½ hour* with piperidine and a 5% aqueous solution of sodium hydroxide; and that the percentages of silicon in the gelatinous matter just referred to depended on the duration of the treatment with acetone and alkali.

This unsuspected instability of the $Si{-}CH_2Ph$ binding towards alkali * is also shown by the fact that when dibenzylsilicol is heated on a water-bath with a 5—10% solution of sodium hydroxide in aqueous acetone during about 30 minutes it is almost completely decomposed with formation of toluene; the gelatinous precipitate obtained by acidifying the solution gave Si, 42·7%, whereas SiO_2 requires Si, 46·9%.

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CLXXXIX.—*The Catalytic Oxidation of Nitro- and Halogen Derivatives of Toluene by Means of Air.*

By EDWARD BRADFORD MAXTED and ARTHUR NORMAN DUNSBY.

BY the oxidation of aromatic hydrocarbons containing a side chain, by means of air in the presence of vanadium compounds, carboxylic acids are obtained as in the wet oxidation with chromic acid or permanganate. For instance, Walter (*J. pr. Chem.*, 1895, **51**, 107) found that benzoic acid, together with benzaldehyde, could be

* It has been previously shown that a compound containing the $Si{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$ group may be decomposed by alkalis, giving toluene-sulphonic acid (Kipping, J., 1908, **93**, 472).

obtained by passing a mixture of toluene vapour and air over heated vanadium pentoxide; and the reaction has more recently received renewed attention with a view to its technical application. The oxidation of alcohols and aldehydes in a similar way is also well known: for instance, Naumann, Moeser, and Lindenbaum (*ibid.*, 1907, **75**, 149) prepared acetic acid and acetaldehyde by leading a mixture of ethyl alcohol vapour and air over vanadium pentoxide in a combustion tube.

It was considered of interest to ascertain whether the method could be extended to substances other than oxy-compounds and hydrocarbons, and, in the work here described, the reaction has been applied to aromatic derivatives containing, in addition to a methyl group, a halogen atom or a nitro-group attached to the nucleus. It was found that the side chain could be oxidised to carboxyl, as in the wet oxidation method, without the splitting off of the halogen or the nitro-group, a fair yield of the corresponding acid being obtained.

EXPERIMENTAL.

The catalyst employed consisted of granular tin vanadate, which was contained in a glass U-tube immersed in a bath of fused sodium and potassium nitrates, the volume of the catalyst space being 10 c.c. in each case. Air, from a reservoir under pressure, was led, at a rate measured by a velocity meter of the constricted tube type, through a small wash-bottle, which contained the substance to be oxidised and acted as a carburettor, and thence through the catalyst tube. The products of oxidation passed into a small tubular receiver, which could be detached for weighing before and after each experiment. The rate of passage of the substance undergoing oxidation was regulated by maintaining the carburettor at a suitable temperature, which was determined by means of preliminary experiments for each substance tested.

Oxidation of p-*Nitrotoluene.*—For the 10 c.c. of catalyst used, a suitable rate of passage of air through the small bubbling tube containing the *p*-nitrotoluene was found to be 10 litres per hour, the carburettor temperature being 80—100°. The product consisted of *p*-nitrobenzoic acid, unchanged *p*-nitrotoluene, and some *p*-nitrobenzaldehyde, and it was sufficiently free from acidic decomposition products—for instance, oxides or oxy-acids of nitrogen—to render possible the determination of the *p*-nitrobenzoic acid content by simple titration. From a filtered alkaline solution of the product, by acidification with hydrochloric acid, pure *p*-nitrobenzoic acid (m. p. 237°; *M*, 167) was obtained.

In order to determine the most suitable catalyst temperature, a series of experiments with a uniform carburettor temperature of

93° was carried out. Under these conditions, with the air at a rate of 10 litres per hour, about 0·3 g. of nitrotoluene passed the 10 c.c. of catalyst per hour. The percentage yields (*a*) of *p*-nitrobenzoic acid are in Table I, *t* denoting the temperature of the catalyst.

TABLE I.

t	260°	270°	275°	280°	285°	290°	310°
a	8·4	14·0	15·0	14·0	16·0	15·6	11·2

It will be seen that the reaction begins below 260°, and that for catalyst temperatures from 270° to 300° the yield remained fairly constant at 14—16%.

The oxidation of *o*-nitrotoluene was also examined; but much decomposition occurred at catalyst temperatures sufficient to cause oxidation, and little or none of the corresponding acid could be isolated.

Oxidation of o-*Bromotoluene*.—Under similar conditions to those used for *p*-nitrotoluene, the following results were obtained with a carburettor temperature of 60°.

TABLE II.

t	255°	265°	275°	285°	290°	295°	300°	305°
a	7·4	12·1	13·7	21·0	24·3	14·0	7·8	6·3

Some hydrogen bromide was also formed by decomposition; but, since *o*-bromobenzoic acid is not very soluble in cold water, it was found possible to correct for this mineral acid by titrating the mixture with standard alkali first in the cold and then boiling, the difference between the two end-points representing bromobenzoic acid. The acid was also isolated in a pure condition and identified. Some *p*-bromobenzoic acid was apparently also present, due probably to *p*-bromotoluene in the material taken for oxidation.

Oxidation of o-*Chlorotoluene*.—*o*-Chlorobenzoic acid was in some experiments obtained in a pure condition, free from water, hydrochloric acid, and unchanged chlorotoluene, by adjusting the temperature of the receiver, the crude reaction product having m. p. 135° and a titration value of approximately 156; but in most cases unchanged chlorotoluene was also condensed.

The percentage yields (*a*) of chlorobenzoic acid obtained in a series of tests, with the carburettor temperature maintained at 60°, are tabulated below.

TABLE III.

t	260°	275°	285°	287°	293°
a	4·9	7·4	13·0	13·8	12·6

In cases in which the product in the receiver was not free from unchanged raw material, the pure chloro-acid could readily be isolated by solution in sodium hydroxide and precipitation with hydrochloric acid.

38, WALLISCOTE ROAD,
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CXC.—*The Influence of Glass upon Vapour Pressure.*

By JACOBUS RINSE.

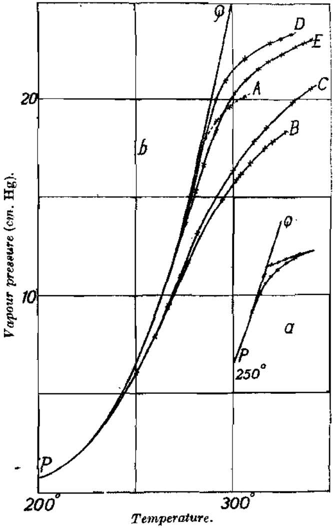
IN determining the dissociation of mercuric iodide by means of glass-spring indicators (*Rec. trav. chim.*, 1928, **47**, 35), we observed that the vapour pressure–temperature curves were of an unusual form : instead of changing abruptly to the linear form on passing the saturation point, as required by Gay Lussac's law, the curves were continuous. Moreover, it was frequently noticed that the vapour pressure at that temperature at which the gas should be just unsaturated was too low—in many cases more than 10% and once 14% below the calculated value. A similar phenomenon has been described by McHaffie and Lenher (J., 1925, **127**, 1559; 1926, 1785; 1927, 272) in the adsorption of water and benzene on glass, quartz, and platinum surfaces. Frazer, Patrick, and Smith repeated and extended these experiments (*J. Physical Chem.*, 1927, **31**, 897), and found continuous curves under certain conditions. These results, however, are probably of a different type from those now to be described.

(*a*) *Reaction between the Glass Wall and Mercuric Iodide.*—The passage to the Gay Lussac curve was continuous if the indicators had been previously heated above 500°; if, however, the indicator was evacuated without being heated during the pumping, a break was obtained immediately after evacuation, as shown in Fig. 1a. If the apparatus was then heated at 600° for 30 minutes, the vapour-pressure curve determined during the subsequent cooling was continuous. Although the glass never appeared to be attacked, even in indicators which had been used for a long time, experiments were made to determine whether an excess of either mercury or iodine was responsible for the continuity, but the results showed that they were not. Moreover, mercurous iodide gave curves showing a break. Further experiments giving negative results on this point are described in section (*d*).

(*b*) *The Influence of Drying.*—As it had been observed that the effect was greatest when the glass-spring indicators had been evacuated and heated simultaneously for a long time, during which

some mercuric iodide distilled off, experiments were made to decide whether adsorbed water had any influence. A manometer was constructed to which a bulb containing fine phosphoric oxide was connected by a wide tube. The apparatus was filled in the same way as for the intensive drying experiments in this laboratory (J., 1926, 2657). The indicator was left for 14 days and occasionally heated. The phosphoric oxide bulb was then removed and the

FIG. 1.



vapour-pressure curve determined: it showed only a continuou transition over a short range, and a second similar experiment ha the same result. Therefore water is probably not the cause of th phenomenon.

(c) *The Influence of Glass.*—Some glass powder (1·68 g.), mad from the same high-melting Jena combustion glass as the indicators was introduced, and the apparatus evacuated during 30 minute and heated meanwhile. The curve subsequently determined i

represented by A (*Fig. Ib*) *and shows a gradual transition over the* range 285—310°. After ½ hour's heating at 560°, curve B was obtained, which shows a much longer range. As a small amount of gas was liberated during the heating (probably it had been adsorbed by the glass powder), the indicator was again evacuated, by breaking a point which was connected by a rubber tube to the pump, and resealed. The volume was thus diminished, whilst the amount of mercuric iodide remained the same as before; accordingly the new vapour-pressure curve C now lies above B. After the determination of C the glass was freed from mercuric iodide by heating the lower part of the manometer. The glass powder was shaken into the end of a tube which was sealed off. Curve D was then obtained, which is much less straight than C. The influence of the glass was therefore distinctly demonstrated. After heating again at 550—600° for 1½ hours, curve E was obtained. The points on all these curves were found both with increasing and with decreasing temperatures, and the equilibrium was established very rapidly.

A second experiment, in which a definite amount of mercuric iodide was used, gave the same results. 1·5 G. of glass powder were placed in an indicator of about 13 c.c. capacity. A part of the iodide sublimed during the evacuation and heating. The normal values of the pressure can be calculated from Gay Lussac's law, and hence the lowering of the vapour pressure was found to be as follows:

Temperature	241°	250°	259·5°	269·5°	276·5°	286·5°	303°
Pressure (calc.)	4·7	6·7	9·0	11·8	14·3	18·0	27·0
,, (obs.)	4·2	5·75	7·35	9·0	10·35	12·7	16·3
Lowering	0·5	0·95	1·65	2·8	3·95	5·3	10·7
Lowering, %	11	14	18	24	27·5	29·5	40

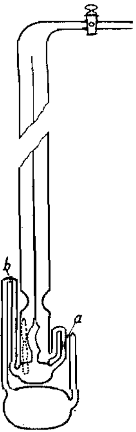
We see from this table that a decrease of 40% can occur. In the same way a lowering of 14% was found when no glass powder was used.

At higher temperatures the decrease diminished till the theoretical curve was reached. This was verified in indicators of known volume with a known amount of mercuric iodide.

For the further investigation of the phenomenon the apparatus shown in Fig. 2 was constructed. The bulbs, of about 30 c.c. capacity, were connected by a tube, in which a capillary was made, and 5 g. of glass powder were introduced in one of them. The apparatus was then evacuated and heated in an electric furnace at 550—600° for ½ hour. After cooling, 200 mg. of mercuric iodide were rapidly placed in the second bulb. The whole was evacuated again, the glass powder heated, and the connecting tube to the pump finally sealed off. The apparatus was again placed in the

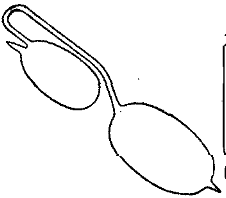
furnace and heated to 600°. Then it was put in a bath of an equimolecular mixture of potassium and sodium nitrates and heated to a temperature at which, as found by calculation, the vapour ought to be just unsaturated. The apparatus was now raised so that the capillary was above the surface of the liquid and could be sealed off, thus separating the bulbs. The volume and weight of mercuric iodide in each were then determined. In this way it was found that the vessel which contained glass powder had more iodide than the other. On one occasion this difference amounted to 12·5%, and in another case to 5·5%. In these experiments it is necessary to evacuate carefully and to heat the glass powder strongly; otherwise, no excess of iodide is found in the vessel with glass powder.

FIG. 3.



To complete these experiments it was desirable to measure the pressure. Fig. 3 shows the apparatus used. The procedure of filling was the same as in the preceding experiments. Glass powder was introduced in the space immediately below the spring, the apparatus was evacuated and heated to 600°, mercuric iodide was introduced, and the apparatus again baked out and sealed at *a*. In Fig. 4, A is the vapour-pressure curve first determined. This is continuous from about 300° to 330°. At 308°, where the pressure is - 27·5 cm., the capillary *b* was raised out of the bath and sealed off. The subsequent vapour-pressure curve B is now much higher than the former and shows less deviation from the third curve in the figure, which is the saturation curve.

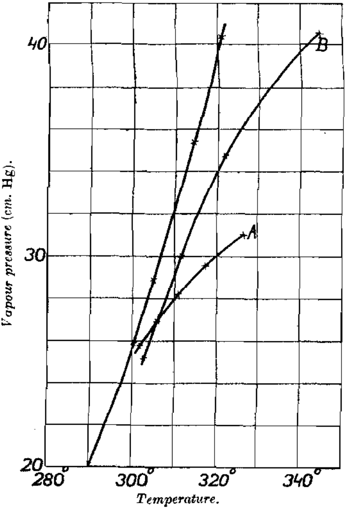
FIG. 2.



This experiment was repeated under more quantitative conditions, glass powder now being placed in the big bulb. This time the manometer was evacuated first through a capillary sealed to the large bulb, and then through the capillary which connected the two sides of the spring. A part of the mercuric iodide, which was introduced in the space immediately below the spring, was distilled off during the second evacuation. The apparatus was then heated to 600°,

after which a continuous vapour-pressure curve was obtained (A, Fig. 5). The bath was then kept constant at 303°, corresponding to the middle of the bend in curve A, and the capillary was brought 1 cm. above the liquid and sealed off, the glass powder thus being separated from the manometer. The new vapour-pressure curve is represented by B (Fig. 5). Then the two parts of the original apparatus were opened and weighed, the volume and weight of

Fig. 4.



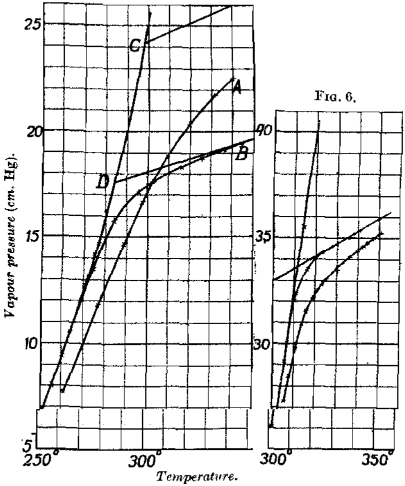
mercuric iodide being determined. From these values the corresponding theoretical curves C and D could be derived, and it is seen that without glass powder the maximum lowering is 10·2% (curves B and D at 285°), and with powder 29·5% (curves A and C at 300°).

(*d*) *The Roughness of the Surface.*—During this investigation the paper of Frazer, Patrick, and Smith appeared (*loc. cit.*), dealing with the thickness of adsorbed vapour films. The authors show that for water and toluene the smoothness of the surface is very important,

the reaction between water and glass being largely responsible for the results of McHaffie and Lenher. With toluene and a plane surface no adsorption could be detected by vapour-pressure determinations.

The roughness of the surface might therefore account for the phenomenon with mercuric iodide. To test this an indicator was made that had not been in contact with water or aqueous vapour; it was blown through a tube containing phosphoric oxide, and then

FIG. 5. FIG. 6.



heated in a stream of very dry oxygen until the glass softened, and is therefore believed to have a plane surface such as Frazer and his co-workers found necessary. Into this apparatus were rapidly introduced 48 mg. of mercuric iodide, which was heated in a vacuum until a part distilled off, and the observations represented in Fig. 6 were made. The higher curve was obtained immediately after the evacuation, and the lower after heating for 2 hours at 580°. The maximum decrease is 12%. This experiment proves that the effect with mercuric iodide cannot be explained in the same way as that

with toluene. Assuming that adsorption has occurred, we can calculate the thickness of the adsorbed vapour layer. The internal surface of the glass-spring indicator used is about 20 sq. cm., the amount of mercuric iodide used in the last case is about 40 mg., and the surface occupied by a mercuric iodide molecule in a layer of the tetragonal crystal is $4{\cdot}4^2 \times 10^{-16}$ sq. cm. (Bijvoet, Claassen, and Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 529; Huggins and Magill, *J. Amer. Chem. Soc.*, 1927, **49**, 2357). Therefore to produce one layer of iodide molecules on the inner surface of the manometer we need $20/4{\cdot}4^2 \times 10^{-16} = 10^{16}$ molecules, *i.e.*, $10^{16} \times 454/6{\cdot}06 \times 10^{23} = 0{\cdot}75 \times 10^{-5}$ g. Since we found a decrease of 12% of 40 mg., about 5 mg. should be adsorbed on the wall, and the thickness of the layer would be $(5 \times 10^{-3})/(0{\cdot}75 \times 10^{-5})$, *i.e.*, more than 500 molecules. Such a result is very improbable, for it cannot be understood why the glass wall should exert its influence on molecules separated from it by so many layers. Hence we may conclude that adsorption is probably not the cause of the behaviour of mercuric iodide.

To determine whether a slight reaction between glass and mercuric iodide was responsible for roughening the glass surface or for the formation of mercury silicate at higher temperatures, the following experiments * were carried out. In a bulb of combustion glass of about 25 c.c. capacity 5·6 g. of powdered glass of the same origin were heated above 600° in a vacuum to remove adsorbed water and air; a known amount of mercuric iodide was rapidly introduced, and the bulb was evacuated again and sealed off. The tube was then heated in an electric furnace at 600—650°, and mercuric iodide was sublimed in the point of the vessel, which was broken off, weighed, heated until all the iodide was driven off, and weighed again.

(1) Introduced 139·4 mg., heated for 24 hours at 650°, regained 139·7 mg.

(2) Introduced 101·8 mg., heated for 20 hours at 600°, regained 101·6 mg.

Since in the experiments with glass-spring indicators the heating was at 550—600° and lasted only for 1 hour, it is evident that not the slightest reaction could have taken place in that case.

(*e*) *Behaviour of Other Substances.*—It was desirable to know if other substances showed similar phenomena when treated in the same way. Accordingly preliminary experiments were made with mercuric chloride and bromide, iodine, mercurous chloride, and

* These two tests were done in the chemical laboratory (Remsen Hall) of the Johns Hopkins University. I am indebted for this part of the work and also for the interest they have taken in this paper to Drs. Patrick and Frazer.

mercury; the first three showed continuous transformations to the Gay Lussac curve, especially mercuric bromide, which showed decreases up to 25% even without glass powder. The other two substances, on the other hand, showed sharp breaks, and no decreases were observed even after heating for some hours at 600°. These experiments are being continued.

Summary.

1. Mercuric iodide exhibits a continuous passage from the saturation curve to the Gay Lussac line, similar to that found by McHaffie and Lenher for water and benzene and by Frazer, Patrick, and Smith for toluene. The deficiencies in vapour pressure for mercuric iodide and certain other substances are, however, much larger.

2. No reaction could be detected between glass and mercuric iodide.

3. The effect is independent of the degree of dryness.

4. The introduction of glass powder into the vessel augments the effect.

5. A plane glass surface does not prevent the phenomenon, contrary to the results of Frazer, Patrick, and Smith with toluene and water.

6. Adsorption cannot explain the phenomenon, for the layers would have to be more than 500 molecules thick, and this is regarded as very improbable.

I take this opportunity to thank Prof. Dr. A. Smits and Dr. J. M. Bijvoet for the interest they have taken in this paper.

UNIVERSITY OF AMSTERDAM. [*Received, October* 31*st*, 1927.]

CXCI.—*Reduction of Nitrites, Nitrates, and Nitric Acid with Magnesium Amalgam: A New Method of Preparing Hyponitrites.*

By PANCHANAN NEOGI and BIRENDRA LAL NANDI.

IT has been shown that magnesium reacts very slowly with solutions of many metallic salts to give hydroxides (Lemoine, *Compt. rend.*, 1899, **129**, 291; Tommasi, *Bull. Soc. chim.*, 1899, **21**, 885; Kahlenberg, *J. Amer. Chem. Soc.*, 1903, **25**, 380; Senbert and Schmidt, *Annalen*, 1892, **267**, 218). Since magnesium amalgam is much more reactive, its reducing action on metallic nitrates and nitrites has now been studied, and found to afford a convenient method for the preparation of hyponitrites. Among those thus prepared are

several not hitherto described, *viz.*, *cadmium, zinc, lithium, rubidium,* and *cæsium hyponitrites,* and that of magnesium has been obtained in solution.

Most of the known hyponitrites depend for their preparation on double decomposition with sodium nitrite (compare Divers, J., 1899, **75**, 95), but the method now described is direct. Moreover, the use of magnesium amalgam possesses advantages over that of sodium amalgam (as used by Divers) in that magnesium hydroxide is much more readily removed than sodium hydroxide and that it does not enter into secondary reactions (*e.g.* precipitation of metallic hydroxides) or tend to decompose unstable hyponitrites.

The reduction of nitrates by magnesium amalgam takes place in several stages, the presence of nitrites, hyponitrites, hydroxylamine, and ammonia having been established in many cases. Hydroxylamine is frequently produced in considerable quantities, but not a trace was observed in the preparation of rubidium and cæsium hyponitrites; its isolation as sulphate in good yield is described.

In testing for hyponitrites by silver nitrate it is first necessary to remove the hydroxylamine by shaking with mercuric oxide. The silver nitrate test may be applied in the case of lithium, sodium, potassium, barium, strontium, and calcium hyponitrites even in the presence of their hydroxides, for the silver oxide first formed reacts with the soluble hyponitrites, precipitating the characteristic yellow silver hyponitrite; but in the case of rubidium and cæsium hyponitrites, the silver oxide does not undergo this double decomposition, and the solution has to be neutralised with dilute nitric or acetic acid before the test is applied.

EXPERIMENTAL.

Preparation of Magnesium Amalgam.—20 G. of magnesium, either as filings or as small pieces of clean ribbon, are placed in a flask containing 400 g. of mercury and gently heated for 2 or 3 minutes on a wire gauze over a flame. The flask is then removed and vigorously shaken at intervals during 10 minutes, the heat evolved being sufficient to keep the elements in a state of reaction. (If heating is continued for too long, the whole mass takes fire.) When all the magnesium has dissolved, the liquid mass is solidified by being poured on a porcelain tile, and while still soft it is cut into small pieces and stored in a stoppered bottle which is protected from moisture. It was found unnecessary and even undesirable to conduct the amalgamation in an atmosphere of carbon dioxide or hydrogen, for the whole mass sometimes took fire in the latter gas.

Procedure.—Owing to the exothermic nature of the reduction and to the instability of hyponitrites, all solutions were immersed

in a freezing mixture and thoroughly stirred during the reaction, so that the temperature did not exceed 5°. Also, it was found essential to continue the reduction until no nitrite remained before attempting to concentrate the solution, for nitrates and nitrites appear to accelerate the decomposition of the hyponitrite.

It is advisable to filter off the bulky precipitate of magnesium hydroxide from time to time during the reduction, for it is difficult to remove it all at once at the end of the reaction.

Lithium Hyponitrite.—To a concentrated neutral solution of lithium nitrate, cooled in an ice-salt mixture, magnesium amalgam was slowly added in small pieces. The mixture was kept for a short time, and the precipitated magnesium hydroxide was filtered off and washed once or twice with small quantities of ice-cold water. The filtrate was again reduced, and the operation repeated until the solution was free from nitrate and nitrite; it then contained ammonium and lithium hydroxides, hydroxylamine, and lithium hyponitrite, but no magnesium salt. The solution was placed in a vacuum desiccator over concentrated sulphuric acid, the hydroxylamine decomposing and the resulting ammonia being absorbed in the acid. After about a fortnight, the whole set to a solid, white mixture of lithium hydroxide and hyponitrite. The hyponitrite was extracted with absolute alcohol, in which it was moderately soluble, and then precipitated with ether. Several repetitions of the extraction and precipitation gave *lithium hyponitrite* free from hydroxide; it was dissolved in the minimal quantity of water and again evaporated to dryness in a vacuum desiccator over sulphuric acid (Found, by conversion into Li_2SO_4: Li, 19·34. $Li_2N_2O_2$ requires Li, 18·79%). The slightly high result was due to hydrolysis during the final crystallisation, as was shown by the alkalinity of the aqueous solution.

Sodium Hyponitrite.—Sodium nitrite (35 g.) in water (200 c.c.) was reduced as above, 420 g. of 5% amalgam being used. The solution smelt strongly of ammonia and contained hyponitrite and hydroxylamine. After 20 days' evaporation the solid hyponitrite was obtained together with caustic soda; the latter was extracted by washing with absolute alcohol, and the hyponitrite dried in a vacuum desiccator. (Divers's method of precipitating the hyponitrite by the addition of absolute alcohol gave a smaller yield.) (Found: Na, 43·63. Calc.: Na, 43·4%).

Potassium Hyponitrite.—The nitrite (40 g. in 250 c.c. of water) was reduced exactly as in the foregoing example. The solution was strongly alkaline and contained ammonia, hydroxylamine, caustic potash, and potassium hyponitrite, and the hyponitrite was worked up as before (Found: K, 56·49. Calc.: K, 56·58%).

Reduction of the nitrate instead of the nitrite proceeded similarly, but was less convenient.

Rubidium Hyponitrite.—Rubidium nitrate solution (from 7 g. of the chloride, by reaction with silver nitrate) was completely reduced as usual: the resulting solution contained rubidium hydroxide and hyponitrite, and ammonia, but no hydroxylamine. After keeping over-night in a vacuum desiccator over sulphuric acid, the solution was neutralised with dilute acetic acid, and then concentrated as before. The resulting long, needle-shaped, colourless crystals were repeatedly washed with absolute alcohol to remove all the acetate, and the *rubidium hyponitrite* was dried in a vacuum desiccator (Found, by conversion into Rb_2SO_4 : Rb, 63·6. $Rb_2N_2O_2,2H_2O$ requires Rb, 64·0%).

The solid hyponitrite was very deliquescent. When heated in a test tube it melted in its water of crystallisation, and decomposed at a higher temperature without explosion.

Cæsium Hyponitrite.—The nitrate (from 5 g. of the chloride) was reduced as before. The solution, containing cæsium hydroxide and hyponitrite, together with ammonia but no hydroxylamine, ultimately yielded a white mass from which alcohol extracted the hydroxide and left the *hyponitrite* (Found : Cs, 56·69. $Cs_2N_2O_2,8H_2O$ requires Cs, 56·54%).

Magnesium Hyponitrite.—This hitherto-unknown hyponitrite has been prepared by us, but not isolated, by reduction of the nitrate (40 g. in 250 c.c. of water). The hyponitrite is found with the precipitated hydroxide and not in the solution. The washed precipitate was added to dilute acetic acid (6%) until no more dissolved and a slight excess remained. The filtered solution gave a positive test for hyponitrite with silver sulphate, but on keeping over-night in a vacuum desiccator, the magnesium hyponitrite was totally decomposed. It was also found that the hyponitrite was not reprecipitated by any alkali, but was decomposed.

That magnesium hyponitrite is soluble in ether and acetic acid has been shown by our attempts to isolate it in organic media. The precipitate of hydroxide and hyponitrite was extracted with a mixture of glacial acetic acid (1 vol.) and ether (6 vols.), and the extract evaporated in a vacuum desiccator to remove the ether. The remaining acetic acid solution responded to the tests for hyponitrites, but further evaporation caused decomposition.

Zinc Hyponitrite.—Reduction of the nitrate (20 g. in 200 c.c. of water, to which a few drops of nitric acid had been added) gave a solution containing hydroxylamine and a little magnesium but no hyponitrite. The precipitate, however, showed the presence of hyponitrite, and was therefore washed, dissolved (with cooling) in

the minimum quantity of dilute acetic acid (6%), neutralised with ammonia, and kept for 2—3 hours; the gelatinous precipitate which separated was filtered off, washed, dissolved in acetic acid, and reprecipitated by neutralisation, the process being repeated five times in order to get rid of magnesium hydroxide and zinc hydroxide. The gelatinous white precipitate ultimately obtained had the appearance of boiled arrowroot and was free from magnesium; on drying in a vacuum desiccator it yielded a white powder (Found, by heating to ZnO: Zn, 45·5. ZnN_2O_2,H_2O requires Zn, 45·6%). *Zinc hyponitrite* explodes on heating unless it is warmed very gently at first.

Cadmium Hyponitrite and Hydroxyhyponitrite.—After reduction of the nitrate in the usual way, the filtered solution contained nitrate, hydroxylamine, and ammonia, but no hyponitrite. The washed precipitate, however, showed the presence of hyponitrite, and was therefore treated as in the case of zinc. The white precipitate which was slowly formed in the neutralised solution was filtered off after 3 hours, washed, redissolved in dilute nitric acid, and again neutralised. After six repetitions of this process, the precipitate was dried and obtained as a yellowish powder of *cadmium hyponitrite* (Found: Cd, 64·8. CdN_2O_2 requires Cd, 65·2%). This had $d_{4^\circ}^{22^\circ}$ 2·121.

During the process of dissolution and reprecipitation, the colour of the hyponitrite gradually changed from white to light yellow. The *white* substance has been found to be the *oxyhyponitrite* [Found: Cd, 70·6. Cd(OH)(NO) requires Cd, 70·5%]. This case is analogous to that of lead hyponitrite (Kirschner, *Z. anorg. Chem.*, 1898, **16**, 424). The basic hyponitrite was very explosive, like silver hyponitrite, so for analysis a weighed quantity was dissolved in concentrated nitric acid in a crucible and cautiously heated to the oxide.

Action of Heat on Cadmium Hyponitrite.—0·2892 G. of the yellow salt was placed in a hard-glass tube, which was exhausted by a Sprengel pump, and heated gradually in a bath of sulphuric acid. At 185° the substance decomposed suddenly into cadmium oxide and a gas, which was collected in a graduated tube and occupied 40 c.c.; as it was almost totally, though slowly, absorbed by cold water, it was assumed to be nitrous oxide, especially as no nitrous fumes were formed when air was admixed with it. The gas was completely soluble in alcohol.

Calcium Hyponitrite.—After reduction of the nitrate as usual, the solution contained hydroxylamine, ammonia, and calcium hyponitrite, but no magnesium. The precipitate also gave tests for hyponitrite. Calcium hyponitrite being partially soluble in water, the precipitate was repeatedly extracted with small quantities of water, and the extract added to the main solution, which was then kept over sulphuric acid in a vacuum desiccator for a day, to remove

hydroxylamine and ammonia, neutralised with phosphoric acid, to remove calcium hydroxide, filtered, and the filtrate was evaporated over sulphuric acid in a vacuum. The solid crystalline mass was washed with small quantities of absolute alcohol and again dried (Found : Ca, 23·17. Calc. for $CaN_2O_2,4H_2O$: Ca, 23·26%).

Strontium Hyponitrite.—This was prepared exactly as in the preceding case (Found : Sr, 37·1. Calc. for $SrN_2O_2,5H_2O$: Sr, 36·9%).

Barium Hyponitrite.—This salt, which is more soluble in water than that of calcium or strontium, was prepared in the same way (Found : Ba, 51·66. Calc. for $BaN_2O_2,4H_2O$: Ba, 50·98%).

Lead Hyponitrite and Oxyhyponitrite.—Reduction of lead nitrate (30 g. in 200 c.c. of water) gave a solution containing hydroxylamine and ammonia, but no magnesium or hyponitrite. The precipitate was dissolved with cold dilute acetic acid, the solution neutralised, and the dissolution and precipitation were repeated. The white precipitate thus formed was filtered off, washed, and dried (Found : Pb, 77·8. Calc. for PbN_2O_2 : Pb, 77·6%).

The white salt, after treatment with acetic acid and ammonia four or five times at room temperature, became yellow; it was then filtered off, washed, and dried in a vacuum (Found : Pb, 84·2. Calc. for PbO,PbN_2O_2 : Ph, 84·5%).

Reduction of Other Nitrates.—In the cases summarised below hyponitrites were not obtained.

1. *Mercuric nitrate* gave a red precipitate of mercuric oxide; ammonia was evolved, and the solution contained magnesium nitrite.

2. *Mercurous nitrate* gave at first a brown precipitate, which gradually turned black; ammonia was evolved and magnesium nitrite was detected in the solution.

3. *Cobalt nitrate* gave at first a blue precipitate (perhaps a basic salt), which gradually turned to brown cobaltic hydroxide; ammonia was evolved and the solution contained magnesium nitrate and nitrite only.

4. *Copper nitrate* gave a precipitate of basic copper nitrate, $Cu(NO_3)_2,3Cu(OH)_2$ (Found : Cu, 52·88. Calc.: Cu, 52·92%), and the solution contained magnesium nitrate and nitrite, hydroxylamine, and ammonia. Nitric oxide is at first evolved, followed by ammonia.

5. *Nickel nitrate* gave at once a black precipitate of nickelic hydroxide, and the contents of the solution were the same as in the preceding case.

6. *Silver nitrate* was at once reduced to the metal; the solution contained magnesium nitrate and nitrite and ammonia.

7. *Ammonium nitrate* gave the nitrite and ultimately ammonia only.

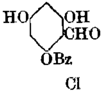
Reduction of Nitric Acid : Preparation of Hydroxylamine Sulphate.—Nitric acid (200 c.c. of 10%) and sulphuric acid (20 c.c. of 10%) were coöled in ice and reduced in the usual way. The precipitate was separated and the filtrate reduced with the addition of 5 c.c. of 10% sulphuric acid, this operation being repeated three times. The solution was finally evaporated on a water-bath, and the hydroxylamine sulphate removed from the magnesium and ammonium sulphates by repeated extraction with warm absolute alcohol. Evaporation of the extract gave hydroxylamine sulphate in a yield of 60% of the nitric acid used; its purity was 97·8% as estimated by Raschig's method.

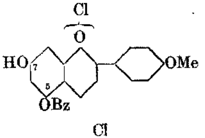
PRESIDENCY COLLEGE, CALCUTTA,
INDIA. [*Received, October 10th, 1927.*]

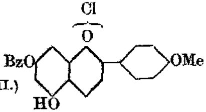
CXCII.—*Experiments on the Synthesis of Anthocyanins. Part IV. The Constitution of* O-*Benzoylphloroglucinaldehyde.*

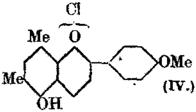
By ALEXANDER ROBERTSON, ROBERT ROBINSON, and ADA MARGARET STRUTHERS.

THE *O*-benzoylphloroglucinaldehyde that is obtained by the monobenzoylation of phloroglucinaldehyde by the Schotten–Baumann method (Robertson and Robinson, J., 1927, 1710) has been found to be a very convenient starting point in syntheses of anthocyanidins and even of certain anthocyanins; it therefore became necessary to determine its constitution. The first indication that the hydroxyl in the *o*-position to the aldehydo-group is the one that is benzoylated and that the derivative has the formula (I) was afforded by the properties of benzoylacacetinidin chloride (II), obtained by condensation of *O*-benzoylphloroglucinaldehyde and *p*-acetylanisole.

(I.) 

 (II.)

(III.) 

 (IV.)

This flavylium salt yielded an alkali-insoluble (therefore not de-benzoylated), red anhydro-base quite similar to those derived from authentic 7-hydroxyflavylium salts, and consequently the formula (III), which is the alternative, seemed improbable. Flavylium salts with one free hydroxyl and that in position 5 give violet or blue anhydro-bases (compare Collie and White, J., 1915, **107**, 369; and see below).

Confirmation of the formulæ (I) and (II) as valid representations of *O*-benzoylphloroglucinaldehyde and benzoylacacetinidin chloride was found in the observations that these substances could be obtained by the condensation of *O*-benzoylphloroglucinol (Fischer, *Annalen*, 1910, **371**, 303) with hydrogen cyanide and anisoyl-acetaldehyde, respectively, in presence of hydrogen chloride. The yield of the aldehyde was poor, but on the other hand isomerides could not be isolated.

The use of diazomethane and of methyl sulphate and sodium hydroxide having proved unsuccessful, we found it possible to methylate *O*-benzoylphloroglucinaldehyde by means of potassium carbonate and methyl iodide in boiling acetone solution. The product was characterised as 2-*benzoyloxy*-4:6-*dimethoxybenz-aldehyde*, $BzO{\cdot}C_6H_2(OMe)_2{\cdot}CHO$, since on hydrolysis it yielded benzoic acid and the known 2-hydroxy-4:6-dimethoxybenz-aldehyde. The method is very suitable for the preparation of this substance.

The benzoylation of phloroglucinaldehyde may be contrasted with that of phloroglucinolcarboxylic acid (Fischer, *loc. cit.*), in which it is the hydroxyl group in the *p*-position to carboxyl that is first attacked. These results can be explained on the assumptions that a carbonyl group cannot inactivate more than one *o*-situated hydroxyl group and that apart from this well-known influence the *o*-hydroxyl is more acidic than the *p*-hydroxyl. Furthermore, the reaction of phloroglucinolcarboxylic acid with benzoyl chloride depends on the formation of a dipotassium derivative, and the application of recognised principles makes it clear that the charge on the bivalent anion will be concentrated first on the carboxyl ion and then on the most remote phenolic oxygen atom; the kationoid carbon atom of benzoyl chloride, therefore, finds electrons available for new co-valency formation most easily at the oxygen atom in the *p*-position to the carboxyl group. Benzoylation of the carboxyl group may also occur, but under the conditions of the reaction the product cannot survive.

EXPERIMENTAL.

4 : 6-*Dihydroxy-2-benzoyloxybenzaldehyde* (I).—In the preparation of *O*-benzoylphloroglucinaldehyde (Robertson and Robinson, *loc. cit.*) the weight of benzoyl chloride employed should be 4·2 g. and not 2·35 g. as previously stated.

A mixture of *O*-benzoylphloroglucinol (E. Fischer, *loc. cit.*) (5·5 g.), anhydrous hydrogen cyanide (5 c.c.), and absolute ether (100 c.c.) was saturated with hydrogen chloride at room temperature. A thick syrup separated in about an hour and after 48 hours the ether was decanted from the semi-crystalline mass that had collected. This was washed with ether, dried in a vacuum, and dissolved in water (100 c.c.) and the solution was heated at 80° for 15 minutes. The red solid that separated appeared to contain benzoic acid; it was dissolved in alcohol (50 c.c.; charcoal), and the solution then added to aqueous sodium bicarbonate (200 c.c.). The crude product was collected and crystallised from chloroform (charcoal) with much loss; only 0·08 g. of the pure substance was obtained. The yield was doubled when the hydrolysis was effected by means of 5% aqueous sodium acetate for 5 minutes at 80°. The aldehyde was obtained in colourless, elongated prisms which darkened at 185°, turned red at 195°, and melted at 198—200° (Found: C, 65·0; H, 4·1. Calc. for $C_{14}H_{10}O_5$: C, 65·1; H, 3·9%). The behaviour on heating was unaltered by admixture with *O*-benzoylphloroglucinaldehyde from phloroglucinaldehyde, and a comparison of crystal form under the microscope and of the ferric chloride reaction (wine-red in alcohol) showed that the specimens were identical. No other product of this reaction could be isolated from the mother-liquors in a homogeneous condition.

2-*Benzoyloxy*-4 : 6-*dimethoxybenzaldehyde*.—A mixture of *O*-benzoylphloroglucinaldehyde (3 g.), acetone (30 c.c.), and methyl iodide (20 c.c.) was boiled, and finely powdered potassium carbonate (15 g.) introduced; the solution was then refluxed for 40 minutes and most of the solvent removed by distillation. Ether and water were added and the ethereal layer was thoroughly washed with fresh water, dried with sodium sulphate, and evaporated. The residue crystallised from ethyl alcohol in long, well-shaped prisms and then from ethyl acetate in colourless, pointed, prismatic needles, m. p. 148° (Found in air-dried material: C, 65·5; H, 5·0. $C_{16}H_{14}O_5,0·5H_2O$ requires C, 65·1; H, 5·1%. Found in material dried at 105° in a high vacuum: C, 67·3; H, 4·4. $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%). The substance is sparingly soluble in alcohol and is unaffected in a short time by boiling aqueous sodium hydroxide. It was also obtained by the action of benzoyl

chloride and warm aqueous sodium hydroxide on 2-hydroxy-4 : 6-dimethoxybenzaldehyde.

Hydrolysis. The benzoate was readily attacked by hot aqueous-alcoholic sodium hydroxide. The product, isolated by acidification and extraction with ether and separated by means of sodium bicarbonate, was 2-hydroxy-4 : 6-dimethoxybenzaldehyde, which crystallised from aqueous methyl alcohol in colourless needles, m. p. 70° (alone or mixed with an authentic specimen). It condensed with ω-methoxyacetoveratrone in presence of hydrogen chloride to a flavylium salt having the properties of *O*-pentamethylcyanidin chloride. The *ferrichloride* had m. p. 210° with previous softening. Acidification of the sodium bicarbonate solution gave benzoic acid.

7-Hydroxy-5-benzoyloxy-4'-methoxyflavylium Chloride (II).—When an ethereal solution of anisoylacetaldehyde (from 4·2 g. of the copper derivative) and *O*-benzoylphloroglucinol (4 g.) at 15° was saturated with hydrogen chloride, a red condensation product quickly separated. On the following day this was collected (5·0 g. or 80%) and dissolved in acetic acid and the solution was saturated with hydrogen chloride. The salt then slowly separated in a crystalline condition and it was recrystallised by solution in a hot mixture of 0·5% aqueous hydrochloric acid and an equal volume of alcohol and addition of concentrated hydrochloric acid until a faint turbidity appeared. The sheaves of orange-red, prismatic needles were dried over sulphuric acid (Found: C, 64·2; H, 4·8. Calc. for $C_{23}H_{17}O_5Cl,H_2O$: C, 64·7; H, 4·5%). The salt exhibited the characteristic properties of the benzoylacacetinidin chloride previously prepared by Pratt, Robertson, and Robinson (J., 1927, 1978) and in addition to a careful direct comparison of the specimens the *picrates* were obtained from both sources and found to be identical in all respects. This derivative separated, when picric acid was added to a boiling alcoholic solution of the chloride, as a mass of curved, hair-fine, orange needles or bundles of needles. It is almost insoluble in hot ethyl alcohol and when heated it darkens at 215° and melts at 230—231° with decomposition. A mixture of the specimens showed the same behaviour.

5-Hydroxy-4'-methoxy-6 : 8-dimethylflavylium Chloride (IV).—A slow stream of hydrogen chloride was passed through a solution of *m*-xylorcylaldehyde (0·8 g.) (Robertson and Robinson, J., 1927, 2202) and *p*-acetylanisole (1·2 g.) in absolute formic acid (40 c.c.) until it was saturated. After 48 hours, the product was precipitated by ether, and crystallised by addition of hot concentrated hydrochloric acid to a solution in hot 4% hydrochloric acid (final concentration 10%); it formed fine, reddish-violet needles (1·2 g.)

which appeared red by transmitted light (Found in air-dried material: C, 58·2; H, 6·2. $C_{18}H_{17}O_3Cl,3H_2O$ requires C, 58·2; H, 6·2%). The substance is dehydrated in a high vacuum over sulphuric acid and becomes deeper red in colour; the product is hygroscopic.

This salt readily forms in dilute hydrochloric acid (up to 10%) orange to deep orange-red solutions. The colour-base precipitated on the addition of sodium acetate to its aqueous solutions dissolves in benzene to a blue solution. When the benzene extract is shaken with dilute hydrochloric acid, it is decolorised and the orange flavylium salt dissolves in the aqueous layer.

Previously the only known 5-hydroxyflavylium salt, not containing hydroxyl groups in other positions, was 5-hydroxy-3 : 3′ : 4′-trimethoxy-6 : 8-dimethylflavylium chloride (Robertson and Robinson, J., 1927, 2204) and this we now find gives a bluish-violet colour-base that is soluble in benzene.

A small amount of tectochrysin (5-hydroxy-7-methoxyflavone) was boiled with acetic anhydride and a little potassium acetate for 30 seconds. An excess of zinc dust was then added and the boiling continued for 30 seconds. The orange-yellow solution was diluted with alcohol (then exhibiting a vivid green fluorescence), filtered, mixed with concentrated hydrochloric acid, and boiled until it became turbid. The deep orange solution obtained was twice extracted with much ether, separated, treated with sodium acetate, and extracted with benzene. The *violet* benzene solution was decolorised on being shaken with dilute hydrochloric acid, the aqueous layer becoming orange; and this alternation could be continued. A similar experiment with 7-hydroxy-4′-methoxyflavone gave a *red* benzene solution and yellow acid aqueous solution. Clearly this behaviour is due to the formation of 5- and 7-hydroxyflavylium salts in the two cases mentioned. The fact that the violet base gives an acid solution having a deeper orange colour than that given by the red base is in harmony with the experience of Collie and White (*loc. cit.*) in connexion with the isomeric benzopyrylium salts derived from orcinol and acetylacetone.

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CXCIII.—*Experiments on the Synthesis of Anthocyanins. Part V. A Synthesis of 3-β-Glucosidylpelargonidin Chloride, which is believed to be identical with Callistephin Chloride.*

By Alexander Robertson and Robert Robinson.

For reasons which have been explained in previous memoirs we were of the opinion that callistephin chloride, one of two anthocyanins isolated by Willstätter and Burdick (*Annalen,* 1916, **412**, 149) from the purple-red aster (*Callistephus chinensis*, Nees, syn. *Aster chinensis*, Linn.), must be regarded as a 3- or 7-glucoside of pelargonidin chloride and the former possibility was preferred. The 3-glucoside (III) has now been synthesised by an unambiguous method and its highly characteristic properties agree so closely with those recorded by Willstätter and Burdick for callistephin chloride that there can be no doubt that the synthetic product is identical with the natural anthocyanin, and thus for the first time an actual flower pigment has been artificially prepared.

In Part I (J., 1926, 1717) we showed in the most favourable case that the general method of the anthocyanidin syntheses of Pratt and Robinson could be applied to the preparation of glucosidoxyflavylium salts. Part II (J., 1927, 242) included a description of the synthesis of a flavylium salt 3-glucoside, but this was not a phloroglucinol derivative; and our many attempts at that stage to produce such a substance were fruitless.

It was more difficult to synthesise the 3-glucosides than the 4′- or 7-glucosides and with the methods then available it was much more difficult to obtain the phloroglucinol derivatives than the corresponding salts with a resorcinol nucleus; the combined difficulty seemed at one time insuperable.

The discovery of the valuable properties of *O*-benzoylphloroglucinaldehyde (see previous paper), with the aid of which a pelargonidin methyl ether 4′-glucoside chloride was synthesised (Part III, J., 1927, 1710), made the prospects much brighter, and after improving the technique of the employment of this substance we ultimately achieved our object.

ω-Chloro-4-hydroxyacetophenone, $HO\cdot C_6H_4\cdot CO\cdot CH_2Cl$, was converted into ω-acetoxy-4-hydroxyacetophenone,

$$HO\cdot C_6H_4\cdot CO\cdot CH_2\cdot OAc,$$

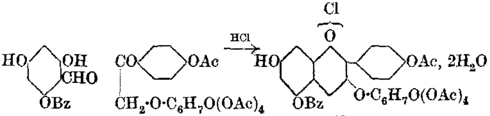
and then by means of aqueous sodium hydroxide into the sparingly soluble sodium salt of ω : 4-dihydroxyacetophenone,

$$NaO\cdot C_6H_4\cdot CO\cdot CH_2\cdot OH.$$

This salt served for the preparation of *carbomethoxy, benzoyl,* and

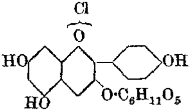
acetyl derivatives, of which only the last, $AcO \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot OH$, was found to serve our purpose through all the subsequent stages.

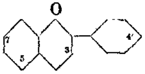
The O-*tetra-acetyl*-β-*glucoside* (I) of this carbinol was obtained by condensation with *O*-tetra-acetyl-α-glucosidyl bromide in presence of silver carbonate in benzene solution at 35°. This method constitutes a considerable improvement in the methods for the preparation of such glucosides and has been used in other cases with satisfactory results. The flavylium salt synthesis by means of *O*-benzoylphloroglucinaldehyde and the glucoside (I) proceeded in ethereal solution and better in a mixture of ether and chloroform.



(I.) (II.)

(III.)





The product (II) was hydrolysed by means of cold 8% aqueous sodium hydroxide, giving a solution of the de-benzoylated and de-acetylated glucoside in a form in which the pyran ring is probably open. On acidification, however, the pyrylium salt is regenerated and without loss of the glucose residue. The purification of the anthocyanin (III) was tedious and difficult; we followed to a large extent the methods of Willstätter and Burdick (*loc. cit.*), but also made use of the picrate. Ultimately we obtained a good specimen of crystalline, homogeneous material, $C_{21}H_{21}O_{10}Cl,2H_2O$, which gave pelargonidin chloride on hydrolysis and had all the properties of callistephin chloride.

This synthesis has a bearing on the problem of the constitution of the anthocyanins, because the recognition of callistephin as a 3-glucoside of pelargonidin debars pelargonenin, an isomeric anthocyanin obtained by Willstätter and Bolton by the step-wise hydrolysis of the diglucoside pelargonin, from being also recognised as a pelargonidin-3-glucoside. The isomerides have widely different properties (see p. 1470) and especially interesting is the fluorescence of alcoholic solutions of pelargonenin chloride and the absence of fluorescence in similar solutions of callistephin chloride. It is

evident also that the situation of the glucose residue in pelargonenin *must be the situation of the diglucoside residue in pelargonin*, because the alkali-colour-reactions of pelargonenin and pelargonin are stated to be very similar (Willstätter and Bolton, *Annalen*, 1915, **408**, 50; 1916, **412**, 136). Pelargonin is also fluorescent in alcoholic solution, although not so brilliantly as pelargonenin.

We are forced to the conclusion that pelargonin chloride is a 5- or 7-diglucoside of pelargonidin chloride, and this is entirely in harmony with the views previously put forward in this and the parallel series of papers dealing with anthocyanidins.

Karrer, Widmer, Helfenstein, Hürliman, Nievergelt, and Monsarrat-Thoms (*Helv. Chim. Acta*, 1927, **10**, 729) have, however, expressed the opinion that the chief anthocyanins, for example, pelargonin, cyanin, peonin, and malvin, are anthocyanidin 3-saccharides and have drawn their conclusions from the results of comparative experiments along three distinct lines, namely (*a*) the properties of malvone, (*b*) the relative yields of derivatives of benzoic acid obtained on oxidation of anthocyanidins and anthocyanins with 15% hydrogen peroxide, and (*c*) the methylation and subsequent fission of anthocyanins.

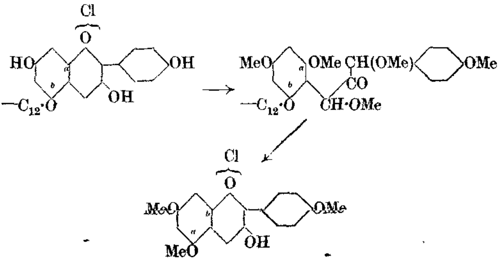
In view of the existence of the anthocyanin hirsutin (Karrer and Widmer, *Helv. Chim. Acta*, 1927, **10**, 758), which may be 3-substituted and resembles malvin in many respects, the colour-reaction evidence is not decisive in this group of delphinidin derivatives. Furthermore the valid interpretation of the oxidation experiments is by no means clear.

Consequently we need discuss only the methylation experiments to which Karrer and Widmer and their collaborators give special prominence. The anthocyanins were methylated by means of methyl sulphate and alkali and then by means of methyl iodide and silver oxide. Hydrolysis of the amorphous product was effected by rather vigorous treatment with hot methyl-alcoholic hydrochloric acid and the resulting methylated anthocyanidin was found to have one free hydroxyl group in position 3. The argument was then developed on the assumption that this position is protected from the action of the methylating agents by the sugar residues.

This is doubtless a plausible and satisfactory interpretation of these interesting observations, but there is also much to be said for an alternative hypothesis founded on the assumption that the sugar groups are attached to position 5.

Under the conditions of the experiments it is highly improbable that the pyran ring could remain intact and when it is broken the three hydroxyls of the phloroglucinol nucleus should be methylated. The recovery of anthocyanidin would then be difficult. Again,

Karrer and his co-workers did not observe *C*-methylation of the phloroglucinol nucleus, and this would certainly have occurred if the pyran ring opened at an early stage. A recent example of this phenomenon is found in the work of Asahina, Shinoda, and Inubuse (*J. Pharm. Soc. Japan*, 1927, 133) on sakuranetin : methyl sulphate and alkali effect the introduction of two or three methyl groups in the phloroglucinol nucleus of the flavanone. The only difficulty met with in explaining Karrer's results by the 5-glucoside structures is that the substances produced by the ring fission of the anthocyanins should be of the form R·CH:C(OH)·CO·R′, and Malkin and Robinson have shown (J., 1925, **127**, 369) that such enols are readily converted into their methyl ethers. The hydroxyl group here considered is the one in position 3, and we must therefore assume that the three carbon atoms connecting the aromatic nuclei take some form, such as ·CH(OMe)·CO·CH(OMe)·, in which the central carbon atom does not bear a methoxyl group. If the possibility of this be granted, then Karrer's results are not in conflict with our hypothesis that the sugar is in position 5. The annexed scheme illustrates a possible course of the reactions.



Summarising, we may say that a consideration of the properties of callistephin and of the reactions of synthetical hydroxyflavylium salts leads to the conclusion that pelargonin (pelargonenin), peonin, and cyanin are 5- or 7-saccharides : Karrer's important experiments are consistent only with the hypothesis that these anthocyanins are 3- or 5-saccharides. It seems, therefore, that the weight of evidence favours the 5-saccharide configuration and in that case the close correspondence in intimate structural detail between the anthoxanthins and anthocyanins breaks down, at least in these instances (compare Atree and Perkin, J., 1927, 234).

EXPERIMENTAL.

ω-*Chloro-4-hydroxyacetophenone*.—The following modification of Tutin's method (J., 1910, **97**, 2503) was adopted in order to avoid the intense irritation of the eyes and skin involved in working with ethereal solutions of the crude ketone.

Chloroacetyl chloride (12 g.) was added in one portion to a mixture of anisole (10 g.), carbon disulphide (50 c.c.), and anhydrous aluminium chloride (30 g.), previously heated under reflux on the steam-bath. The solvent was removed by distillation, and the residue heated for 4 hours on the steam-bath and then decomposed by ice and dilute hydrochloric acid. The solid product was dissolved in the minimum volume of methyl alcohol and added in a thin stream to 10% sodium carbonate solution (300 c.c.); the mixture was agitated for an hour, treated with charcoal, and acidified with hydrochloric acid. The ketone was then crystallised from 80% alcohol (yield, 7—8 g.; m. p. 148°).

ω : 4-*Diacetoxyacetophenone*.—This substance was obtained by Nolan, Pratt, and Robinson (J., 1926, 1968) by acetylation of ω-acetoxy-4-hydroxyacetophenone; it may be more conveniently prepared by heating a mixture of ω-chloro-4-hydroxyacetophenone (6 g.), anhydrous potassium acetate (3 g.), and acetic anhydride (30 c.c.) on the steam-bath for 2 hours (yield, 6·5 g.). It crystallised from light petroleum in elongated, pointed prisms and from benzene in diamond-shaped plates, m. p. 98° (as previously stated, *loc. cit.*).

ω-*Acetoxy-4-hydroxyacetophenone*.—The m. p. of this derivative (Nolan, Pratt, and Robinson, *loc. cit.*) has been raised 6°. The best conditions for its preparation are the following: A mixture of ω-chloro-4-hydroxyacetophenone (35 g.), anhydrous potassium acetate (30 g.), acetic acid (10 c.c.), and absolute ethyl alcohol (250 c.c.) was refluxed for 1 hour, and the greater part of the solvent then removed by distillation. Water (600 c.c.) was added, and the solid collected (32 g.) after the whole had been kept for 12 hours in the ice-chest.

The derivative crystallises from warm water (charcoal) in long, colourless, prismatic needles, m. p. 133°. It is soluble in dilute aqueous sodium carbonate.

ω : 4-*Dihydroxyacetophenone*.—ω-Acetoxy-4-hydroxyacetophenone (32 g.) was added to 16% aqueous sodium hydroxide (150 c.c.), and a clear solution resulted after 15 minutes' heating on the steam-bath. On cooling, the sodium derivative crystallised in glistening plates; it was collected, washed with alcohol, and dried (25 g.). Acetylation by means of acetic anhydride and sodium

acetate for 1 hour at 100° afforded ω : 4-diacetoxyacetophenone, m. p. 98°.

ω-Hydroxy-4-methylcarbonatoacetophenone,

$CO_2Me{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OH$.

—A solution of the sodium salt of ω : 4-dihydroxyacetophenone (5·5 g.) in warm water (50 c.c.) was rapidly cooled in order to cause the separation of small crystals. Methyl chloroformate (2·5 g.) was then gradually introduced with vigorous stirring. After ½ hour the mixture was cooled to 0° and the fine needles that had separated were collected (5·0 g.). The substance was crystallised from benzene–light petroleum (1 : 3), and then separated from water (charcoal) in long, colourless, prismatic needles, m. p. 84° (Found : C, 57·1; H, 4·7. $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8%). This carbonate is readily soluble in alcohol, moderately readily soluble in cold benzene and hot water, and sparingly soluble in light petroleum.

ω-Hydroxy-4-acetoxyacetophenone.—Acetic anhydride (10 c.c.) was added in three portions with vigorous shaking to a suspension of the sodium salt of ω : 4-dihydroxyacetophenone (10 g. finely powdered) in water (40 c.c.) and ether (75 c.c., to which further quantities were added as the product crystallised). After separation the aqueous layer was saturated with sodium chloride and twice extracted with ether; water (20 c.c.) was then added to the combined extracts and the original ethereal layer, and the ether distilled. The residual liquid deposited a white crystalline mass (7 g.), which was sufficiently pure for many purposes. The substance crystallised from water in rectangular, plank-shaped, white prisms, m. p. 95—96°, exhibiting a strong tendency to form clusters (Found : C, 61·8; H, 5·1. $C_{10}H_{10}O_4$ requires C, 61·9; H, 5·2%). The solubilities resemble those of the carbonate (above); the pure substance is sparingly soluble in dry ether. Further acetylation yielded ω : 4-diacetoxyacetophenone, m. p. 98°, and the substance is distinguished from the isomeric ω-acetoxy-4-hydroxyacetophenone by its insolubility in cold dilute alkali solution.

ω-Hydroxy-4-benzoyloxyacetophenone.—Benzoyl chloride (4 g.) was gradually added to a vigorously agitated solution of the sodium salt of ω : 4-dihydroxyacetophenone (5 g.) in water (100 c.c.). After 15 minutes, saturated, aqueous sodium bicarbonate (100 c.c.) was introduced and after 2 hours the solid was isolated (4 g.); it crystallised from ethyl alcohol in glistening, regular, rectangular plates, m. p. 140—141° (Found : C, 70·7; H, 4·6. $C_{15}H_{12}O_4$ requires C, 70·4; H, 4·6%). The substance is sparingly soluble in cold alcohol, moderately readily soluble in cold benzene, and readily soluble in hot alcohol and benzene.

ω : 4-*Dibenzoyloxyacetophenone.*—Benzoyl chloride (4·0 g.) was added in one portion to a vigorously stirred solution of the sodium salt of ω : 4-dihydroxyacetophenone (3·5 g.) and sodium hydroxide (2·5 g.) in water (80 c.c.), and the solid was isolated after 30 minutes and washed with aqueous sodium bicarbonate. This derivative is much more sparingly soluble in hot alcohol than the monobenzoate and crystallised in glistening, diamond-shaped plates, m. p. 180—182° after softening at 176° (yield, 2 g.) (Found: C, 73·3; H, 4·2. $C_{22}H_{16}O_5$ requires C, 73·3; H, 4·4%).

ω-O-*Tetra-acetyl-β-glucosidoxy-4-benzoyloxyacetophenone*,

$$COPh·O·C_6H_4·CO·CH_2·O·C_6H_7O(OAc)_4.$$—

Freshly prepared, dry silver carbonate (10 g.) was added to a solution of ω-hydroxy-4-benzoyloxyacetophenone (4·5 g.) and *O*-tetra-acetyl-α-glucosidyl bromide (12 g.) in dry benzene (80 c.c.) at 35°. The mixture was vigorously stirred for 15 minutes and then refluxed for 30 minutes. The crude glucoside was precipitated from the filtered solution by means of light petroleum (400 c.c.) and the syrup was washed with hot water and triturated with cold water until it became semi-solid. A solution of this material in warm methyl alcohol deposited the glucoside as an opaque jelly which gradually crystallised; the substance then separated from ethyl alcohol in voluminous, colourless, hair-fine needles, m. p. 147° (yield, 5 g.) (Found: C, 59·4; H, 4·9. $C_{29}H_{30}O_{13}$ requires C, 59·4; H, 5·0%). This substance is readily soluble in hot methyl or ethyl alcohol and on cooling separates as a gel that is slowly resolved into crystals; it is sparingly soluble in ether, but easily soluble in cold chloroform. Attempts to condense this glucoside with *O*-benzoylphloroglucinaldehyde to give a derivative of callistephin were unsuccessful.

ω-O-*Tetra-acetyl-β-glucosidoxy-4-acetoxyacetophenone* (I).—The method previously employed for the preparation of ω-*O*-tetra-acetylglucosidoxyacetophenone (J., 1927, 244) was tried, but did not give satisfactory results in the present case.

Dry silver carbonate (15 g.) was added to a solution of ω-hydroxy-4-acetoxyacetophenone (7 g.) and *O*-tetra-acetyl-α-glucosidyl bromide (20 g.) in anhydrous benzene (100 c.c.) at 35°, and the mixture agitated for ½ hour. The reaction proceeded smoothly with a slight rise of temperature and was completed by refluxing for 15 minutes. The filtered solution was mixed with light petroleum (1000 c.c.) and the pale straw-coloured syrup obtained was well washed with hot water and then with cold water until it crystallised. The substance separated from 70% methyl alcohol (charcoal) in long, colourless, rectangular rods, m. p. 132° (yield, 10 g.) (Found: C, 54·8; H, 5·5. $C_{24}H_{28}O_{13}$ requires C, 55·0; H, 5·3%). This

glucoside is very sparingly soluble in anhydrous ether, somewhat readily soluble in the simple alcohols and benzene, and readily soluble in chloroform.

ω-*O*-Tetra-acetyl-β-glucosidoxyacetophenone (*loc. cit.*) was prepared in a similar manner from benzoylcarbinol (10 g.), *O*-tetra-acetylglucosidyl bromide (25 g.), and silver carbonate (20 g.). The product crystallised from 85% methyl alcohol (charcoal) in white, prismatic needles, m. p. 104—105° (yield, 12 g.), and was identical with the specimen previously obtained.

ω-O-*Tetra-acetyl-β-glucosidoxy-4-methoxyacetophenone*,

$MeO{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}C_6H_7O(OAc)_4$.—

This glucoside (4 g.) was obtained in the like manner from anisoylcarbinol (5 g.). It crystallised from 80% methyl alcohol in elongated prisms with pointed ends, m. p. 133° (Found: C, 55·6; H, 5·7. $C_{23}H_{28}O_{12}$ requires C, 55·6; H, 5·6%). The substance is moderately readily soluble in cold alcohol and benzene and sparingly soluble in ether.

Numerous analogies are available indicating that the silver carbonate method applied to *O*-tetra-acetyl-α-glucosidyl bromide (the ordinary acetobromoglucose) yields β-glucosides. A recent example is the synthesis of amygdalin (Campbell and Haworth, J., 1924, **125**, 1337). The use of a higher temperature than the normal, as in the above cases, effects a considerable improvement in the yields. The possibility that these glucosides obtained from benzoylcarbinols are really derivatives of the α-hydroxyphenylacetaldehydes is excluded by their condensation with *o*-hydroxybenzaldehydes to flavylium salts.

3-O-*Tetra-acetyl-β-glucosidoxy-7-hydroxy-5-benzoyloxy-4′-acetoxyflavylium Chloride* (II).—A solution of ω-*O*-tetra-acetyl-β-glucosidoxy-4-acetoxyacetophenone (1·0 g.) and 2-benzoyloxy-4 : 6-dihydroxybenzaldehyde (1·5 g.) in dry chloroform (30 c.c.) and dry ether (100 c.c.) was saturated with dry hydrogen chloride at room temperature and protected from the access of moisture. In the course of 24 hours the liquid became deep red and exhibited an intense orange-green fluorescence. The condensation product crystallised on the sides of the vessel in red plates having a brilliant green reflex; it was collected after 3 days, washed with ether, and air-dried (0·4 g.) (Found: C, 55·8; H, 4·8. $C_{38}H_{35}O_{11}Cl,2H_2O$ requires C, 55·7; H, 4·8%). The original, decanted chloroform–ethereal solution gave a further 0·6 g. of more crude material when it was mixed with dry ether (100 c.c.), and in preparing larger quantities of this salt an equal volume of ether was added to the reaction product without first separating the red crystalline deposit. Recrystallisation was not a feasible operation. The salt is readily

soluble in alcohol to an orange-red solution exhibiting green fluorescence, and it is insoluble in cold 0·5% hydrochloric acid. The alcoholic solution gives a purplish-violet coloration with sodium hydroxide or concentrated aqueous sodium carbonate, but only a yellowish-red coloration with dilute aqueous sodium carbonate. We attribute this behaviour to the necessity for hydrolysis of the 4′-situated acetoxyl group as a preliminary to the exhibition of a strong alkali colour-reaction.

3-β-*Glucosidylpelargonidin Picrate*.—The crude benzoylpenta-acetylglucosidylpelargonidin chloride (4·5 g.) was finely powdered and added to 8% sodium hydroxide solution (90 c.c.), cooled to 10°. Air was excluded from the apparatus by nitrogen, and the solid quickly dissolved to a dark reddish-brown, almost black, solution. After remaining for 3 hours at room temperature, the solution was acidified with 7% hydrochloric acid so that the concentration of hydrogen chloride was brought to 2%. The liquid immediately assumed a deep red colour and was heated at 60° until the formation of the oxonium salt appeared to be complete. Benzoic acid and other ether-soluble impurities were removed by five extractions and, on keeping, the separated aqueous solution deposited some tarry matter. The filtered liquid was evaporated over potassium hydroxide in a good vacuum at the ordinary temperature; more tar separated after 12 hours and was removed. The crude glucoside separated on further evaporation as a red gelatinous mass, which was collected and dried in the air. The product from three experiments was dissolved in 0·05% aqueous hydrochloric acid and precipitated by the addition of an excess of lead acetate solution. The mixture of the lead salt of the glucoside and lead chloride was collected, washed with 0·05% hydrochloric acid (100 c.c.), drained, and added to acetic acid (100 c.c.), which left the lead chloride undissolved. The solution was filtered, and the lead salt precipitated by the addition of ether (500 c.c.) as a dark red sticky mass, which after decantation of the mother-liquor was washed with fresh ether. The residual lead salt was then decomposed by means of propyl alcohol (150 c.c.) and 25% methyl-alcoholic hydrogen chloride (25 c.c.), and the lead chloride removed by filtration. On the addition of dry ether (1000 c.c.) the anthocyanin chloride was precipitated in an amorphous condition as a bright red solid (yield, 1·2 g.). At this stage the hydrochloride could not be crystallised, but it exhibited the correct reactions.

The salt was dissolved in 0·01% hydrochloric acid (10 c.c.), and cold saturated aqueous picric acid (70 c.c.) added. After 24 hours the bright red precipitate was collected, washed with saturated aqueous picric acid, and dried (1·2 g.). The product had a dull

golden reflex. Another specimen was prepared by the addition of aqueous picric acid to an alcoholic solution of the crude chloride.

The salt dissolved with difficulty in boiling alcoholic picric acid (saturated in the cold) and separated gradually in the course of 3—4 days from the cooled solution as a mass of irregular, bright red plates having a brilliant golden reflex. On recrystallisation from more dilute alcoholic picric acid (4 vols. of alcohol mixed with 1 vol. of cold saturated alcobolic picric acid) perfect, microscopic, rectangular plates were obtained; the separation occupied 3—4 days in this case also. The derivative was once more crystallised and washed with alcoholic picric acid and then with ether (Found: N, 6·0. $C_{27}H_{23}O_{17}N_3$ requires N, 6·35%). The salt is moderately readily soluble in ethyl alcohol and readily soluble in methyl alcohol and water. The alcoholic solutions are red in colour, tinged with violet, and become more orange on dilution with alcohol.

3-β-*Glucosidylpelargonidin Chloride* (*Callistephin Chloride*) (III).—The pure crystalline picrate (0·8 g.) was dissolved in 5% methyl-alcoholic hydrogen chloride (35 c.c.), and the chloride precipitated as an amorphous red solid by the addition of ether (300 c.c.). This material (0·5 g.) could be crystallised, by the method described by Willstätter and Burdick (*loc. cit.*) for callistephin chloride, by the slow evaporation of a methyl-alcoholic solution to which one-quarter of its volume of 12% hydrochloric acid had been added. The anthocyanin crystallised in hair-fine, orange-red needles and it was recrystallised in the same manner and obtained in the same form. The crystals are voluminous, filling the liquid and matting together on the filter. In mass they have a dark brownish-red colour and bronze reflex, but are orange by transmitted light under the microscope. A specimen was washed with 12% hydrochloric acid and dried in the air (Found: C, 49·9, 49·8; H, 5·2, 5·0; Cl, 7·1; loss at 105° in a high vacuum, 7·1, 7·2. Calc. for $C_{21}H_{21}O_{10}Cl,2H_2O$: C, 49·9; H, 5·0; Cl, 7·1; $2H_2O$, 7·1%. Found in anhydrous material: C, 53·8, 53·7; H, 4·8, 4·8. Calc. for $C_{21}H_{21}O_{10}Cl$: C, 53·8; H, 4·5%). Willstätter and Burdick record concordant analyses of anhydrous callistephin chloride (C, 53·84; H, 4·61%), but in regard to the air-dried material they merely give the loss at 105° (8·05%), which is between that calculated for $2H_2O$ (7·1%) and $2·5H_2O$ (8·8%).

Every statement made by Willstätter and Burdick (*loc. cit.*, p. 161) regarding the properties of callistephin chloride applies to the synthetic glucoside and therefore there can be no doubt that the substances are identical. The annexed table illustrates this and also the contrast with the isomeric pelargonenin chloride, the

properties of which have been recorded by Willstätter and Bolton (*loc. cit.*).

Callistephin chloride. 3-β-Glucosidyl-pelargonidin chloride.	Pelargonenin chloride.
Dark brown-red mass of hair-fine needles with bronze reflex.	Scarlet-red needles.
Readily soluble in water to a yellowish-red solution that becomes more violet on dilution and then colourless.	Sparingly soluble in water.
Readily soluble in 0·5%, 7%, and moderately readily soluble in 10%, aqueous hydrochloric acid; much less readily soluble in 12% hydrochloric acid.	Very difficultly soluble in 0·5% hydrochloric acid or acid of greater concentration.
When concentrated solutions in aqueous hydrochloric acid are kept, the anthocyanin separates as a gelatinous mass.	
Readily soluble in 7% sulphuric acid.	Sparingly soluble in 7% sulphuric acid.
Easily soluble in methyl alcohol containing hydrogen chloride.	Easily soluble in methyl alcohol.
Easily soluble in ethyl alcohol.	Moderately readily soluble in ethyl alcohol.
The alcoholic solutions are red, tinged with violet, and much yellower than pelargonidin solutions.	Colour of alcoholic solutions intermediate between those of callistephin and pelargonidin.
The alcoholic solutions do not exhibit any fluorescence and give no ferric chloride colour reaction.	The alcoholic solution exhibits strong fluorescence.
Moderately concentrated aqueous acid solutions are yellowish-red and dilute solutions are reddish-yellow.	The acid aqueous solutions have a more bluish tinge.
With aqueous sodium carbonate a reddish-violet to violet-red solution is obtained. The same colour is produced by sodium hydroxide and even in alcoholic solution the colour is reddish-violet, only a shade bluer than in aqueous solution.	Aqueous sodium carbonate gives a violet-blue coloration and in alcoholic solution the coloration is pure blue.

A specimen of pure callistephin chloride was unfortunately not available for a direct comparison, but Professor R. Willstätter very kindly sent us a specimen of partly purified material (" kugeln ") and in addition some asterin chloride. The callistephin specimen gave a ferric chloride reaction (due to asterin) and its alkali-colour reaction was bluer than that of our synthetic glucoside. We therefore took a dilute methyl-alcoholic solution of the latter (containing a trace of hydrochloric acid) and added a solution of asterin chloride of the same concentration in the same faintly acid methyl alcohol, drop by drop; a solution was finally obtained which had exactly the same colour and behaviour with ferric chloride and sodium carbonate as a solution of the crude callistephin (also in the faintly acid methyl alcohol).

Distribution Number.—Willstätter and Burdick state that the partition of callistephin chloride between amyl alcohol and 0·5% hydrochloric acid characterises it as a normal monoglucosidic anthocyanin, but did not determine the distribution number. The synthetic glucoside exhibits an unusually high number. This was determined according to the method of Willstätter and Zollinger (*Annalen*, 1916, **412**, 208). The air-dried pigment was employed and a standard was prepared from 2·130 mg. dissolved in methyl-alcoholic hydrochloric acid (1 c.c.) and made up to 50 c.c. with amyl alcohol previously saturated with 0·5% aqueous hydrochloric acid. The pigment (10·023 mg.) was dissolved in 0·5% hydrochloric acid and shaken with pyridine-free amyl alcohol previously brought into equilibrium with 0·5% hydrochloric acid. It was found useful to clear the solutions centrifugally before making the colorimetric observations; these showed that 31·9% of the total colouring matter had passed into the amyl-alcoholic layer. On a second extraction 32·1% of the material remaining in the aqueous solution passed into the amyl alcohol. The distribution number is therefore 32.

It is difficult to criticise this value because of the paucity of data relating to monoglucosidic anthocyanins. Willstätter and Bolton found the value 19·5 for chrysanthemin (*Annalen*, 1916, **412**, 146). The distribution is visibly affected by the strength of the aqueous acid, and especially in the presence of picric acid a much larger proportion of the glucoside passes to the amyl-alcoholic layer.

Absorption.—The solvent employed was 98% alcohol (475 c.c.) mixed with 20% hydrochloric acid (25 c.c.). The following observations were made through a thickness of 10 cm.: *N*/5000, end of band at 5825; *N*/10,000, at 5757; *N*/20,000, at 5690, and, on addition of ammonia, shift to 6138; *N*/40,000, 5598 (fairly sharp) . . . 4660 (indefinite); *N*/80,000, 5500 (not sharp) . . . 4865—4790. At *N*/40,000 the light admitted in the blue region is of feeble intensity, but at *N*/80,000 the band is obvious.

Hydrolysis.—An equal volume of concentrated hydrochloric acid was added to a boiling solution of the glucoside in 0·5% hydrochloric acid, and after the mixture had been maintained at the point of incipient ebullition for about a minute crystals began to separate; thereafter the solution was soon almost decolorised. The salt was collected, washed with 1% hydrochloric acid, and dried at 80—90° in the air (Found: C, 56·1, 56·1; H, 4·0, 4·1. Calc. for $C_{15}H_{11}O_5Cl,H_2O$: C, 55·6; H, 4·0%). A somewhat high carbon content has previously been observed in pelargonidin chloride hydrate (compare Willstätter and Zechmeister, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1914, 886; Pratt and Robinson, J., 1924, 125,

188). In every respect this substance exhibited the recorded properties of pelargonidin chloride and it was shown by careful comparison of reactions, solubility, and crystal form to be identical with a specimen, prepared from benzoylpelargonidin chloride, which we hope to describe in detail in a later paper.

We wish to thank the Chemical Society and the Royal Society for grants which have defrayed a part of the cost of this investigation.

THE UNIVERSITY, MANCHESTER. [*Received, March 27th*, 1928.]

CXCIV.—*Neocyanine.*

By FRANCES MARY HAMER.

ALMOST all the important photographic sensitisers belong to the cyanine group of dyes and no fewer than sixteen types of cyanines have been described, for fifteen of which the constitution is known: ψ-cyanine, *iso*cyanine, cyanine, 2 : 2′-carbocyanine (pinacyanol), 2 : 4′-carbocyanine (dicyanine), 4 : 4′-carbocyanine (kryptocyanine), thiocyanine, thiocarbocyanine, thio-ψ-cyanine, thio*iso*cyanine, oxacarbocyanine, indocarbocyanine, indo-ψ-cyanine, xanthoapocyanine, and erythroapocyanine (compare Bloch and Hamer, *Phot. J.*, 1928, **68**, 21). Neocyanine is the sixteenth.

Neocyanine is the name given to a dye which Dundon, Schoen, and Briggs isolated as a less soluble by-product in the preparation of kryptocyanine (*J. Opt. Soc. Amer.*, 1926, **12**, 397). They describe in detail its optical and photographic properties, which are particularly interesting, and state that it sensitises more powerfully beyond 8000 Å. than any dye previously reported; since the publication of their paper, it has been recorded that a substance called "prozyanol," of which neither the origin nor the constitution is mentioned, possesses a sensitising maximum still further in the infra-red (Blunck, *Astr. Nachr.*, 1928, **231**, 338). Since Dundon, Schoen, and Briggs have given no details for the preparation of neocyanine, and since no suggestion has been made as to its constitution, it seems desirable to publish what further information is elsewhere available.

1 : 1′-Diethyl-4 : 4′-carbocyanine iodide, or "kryptocyanine," was originally prepared in 9% yield by treatment of an alcoholic solution of lepidine ethiodide with alkali and formaldehyde or chloroform (Adams and Haller, *J. Amer. Chem. Soc.*, 1920, **42**, 2661), and it was presumably according to this method that neocyanine was originally obtained. The constitution of kryptocyanine was

established by Mills and Braunholtz, who synthesised it from lepidine ethonitrate by the action of di-*o*-formylethylamino-diphenyl disulphide, and obtained a 15% yield of pure iodide (J., 1923, **123**, 2804). A general method for the preparation of carbocyanine dyes, by the action of ethyl orthoformate in the presence of pyridine on quaternary salts containing reactive methyl groups, has recently been described: it was applied to the preparation of three 4 : 4′-carbocyanines and, as the yields varied from 36 to 43% of those theoretically possible, its success was regarded as especially striking in this case (Hamer, J., 1927, 2796). It is recorded that in addition to a 42% yield of recrystallised 1 : 1′-diethyl-4 : 4′-carbocyanine iodide, there was also obtained about half its weight of neocyanine, which was identified by its optical and photographic properties.

Three dyes of the neocyanine type have now been prepared by this general method. Since the neocyanine is in each instance less soluble than the corresponding kryptocyanine, it may readily be obtained pure by boiling the mixture of dyes with successive quantities of spirit insufficient for complete solution and, so soon as the colour of the filtrate shows the absence of kryptocyanine, recrystallising the undissolved residue of neocyanine. By the action of pyridine and ethyl orthoformate on lepidine ethiodide, the yield of recrystallised 1 : 1′-diethyl-4 : 4′-carbocyanine iodide obtained was 42%, and that of *neocyanine ethiodide* was 17%. But by carrying out the condensation with lepidine etho-*p*-toluenesulphonate, under slightly modified conditions, the yield of 1 : 1′-diethyl-4 : 4′-carbocyanine iodide was only 7%, whereas that of neocyanine ethiodide was 26% of that theoretically possible. By treatment of the reaction mixture with sodium bromide instead of potassium iodide, *neocyanine ethobromide* was isolated, and this was found more convenient to deal with on account of its greater solubility; in this case the yield of recrystallised 1 : 1′-diethyl-4 : 4′-carbocyanine bromide was 5%, and a 37% yield of neocyanine ethobromide was obtained. When lepidine methiodide is condensed with ethyl orthoformate in pyridine solution, the sole product is 1 : 1′-dimethyl-4 : 4′-carbocyanine iodide (Hamer, *loc. cit.*). By carrying out the condensation with lepidine metho-*p*-toluenesulphonate, isolating the resulting sulphonates, and converting them into bromides, there were obtained a 14% yield of 1 : 1′-dimethyl-4 : 4′-carbocyanine bromide and a 41% yield of *neocyanine methobromide*. From condensations carried out with lepidine etho-*p*-toluenesulphonate, it appears that in the presence of much pyridine there is a tendency to the formation of kryptocyanine rather than of neocyanine, but that with a small amount of pyridine the reverse is the case.

Each of the three neocyanines exhibits a higher melting and decomposition point than does the corresponding 4 : 4′-carbocyanine. This fact, in conjunction with the slight solubility of the neocyanines as compared with the 4 : 4′-carbocyanines, indicates that the neocyanines are compounds of greater molecular weight. The crests of the absorption and sensitising bands of the neocyanines lie nearly 1000 Å. further into the red than those of the 4 : 4′-carbocyanines, from which it may be concluded, either that neocyanine possesses a longer carbon chain connecting the nitrogen atoms than does kryptocyanine, or that it is a substance of greater complexity of structure and higher molecular weight.

After the three neocyanines had been dried in a vacuum at 100—120° until of constant weight, analyses were made, and the empirical formulæ were calculated. The ratio of halogen atoms to nitrogen atoms was in each case 2 : 3. The molecule is very large, so that it is not possible to determine the number of carbon atoms with absolute certainty from the analytical results. With the ethiodide and ethobromide the mean values found for the number of carbon atoms are 37·8 and 36·9 respectively, and with the methobromide the mean is 34·7. It is clear that the neocyanine molecule is formed from three molecules of lepidine alkyl halide, with elimination of one halogen atom, presumably in the form of hydrogen halide, which would combine with the pyridine, and the analyses indicate two possibilities: that either one or two additional carbon atoms may enter into the new molecule. It has not been found possible to formulate the course of the reaction on the second hypothesis. On the other hand, it seems extremely probable that three molecules of lepidine alkyl halide would, through their reactive methyl groups, condense with one molecule of ethyl orthoformate, the process simply consisting in the production of three molecules of ethyl alcohol and being accompanied by removal of hydrogen halide. But formula (I) is not regarded as representing the constitution of neocyanine, for it is only reasonable to suppose that the colour and sensitising properties of neocyanine are attributable to causes similar to those obtaining in kryptocyanine, and that the dyes must in fact bear a very close structural relationship to each other. Now in certain cyanine condensations, two atoms of hydrogen are eliminated per mol. of dye formed. For instance, the preparation of an *iso*cyanine, by the action of sodium ethoxide on an alcoholic solution of quinoline ethiodide and quinaldine ethiodide, is represented by the equation:

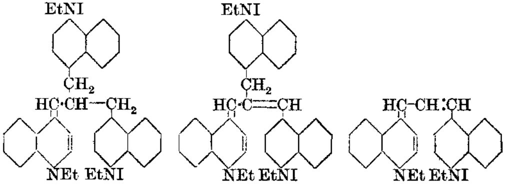
$$C_9H_6N(EtI){\cdot}CH_3 + C_9H_7N(EtI) = C_9H_6NEt{:}CH{\cdot}C_9H_6N(EtI) + HI + H_2.$$

Similarly the preparation of pinacyanol by the action of alkali on an

alcoholic solution of quinaldine ethiodide and formaldehyde, in the *presence of quinoline ethiodide, is accompanied by the loss of two* hydrogen atoms :

$$2C_9H_6N(EtI)\cdot CH_3 + CH_2O =$$
$$C_9H_6NEt{:}CH\cdot CH{:}CH\cdot C_9H_6N(EtI) + H_2O + HI + H_2.$$

It is therefore probable that the same phenomenon takes place in the formation of neocyanine, and that the trilepidylmethane derivative (I) loses two hydrogen atoms, so that neocyanine ethiodide may be represented by formula (II). According to this, it is very simply related to 1 : 1′-diethyl-4 : 4′-carbocyanine iodide (III),



(I.) (II.) (III.)

since it is derived from it merely by substitution of a lepidyl ethiodide group for the hydrogen atom attached to the central carbon atom of the three-carbon chain. This formula, which is proposed for neocyanine, accords with the method of synthesis of the compound, and accounts for its optical and photographic properties, and also explains the slight solubility and high melting point of the neocyanines. It shows reasonable agreement with the analytical results. The question of the presence or absence of the two hydrogen atoms is of course not one that can be decided by analytical data in the case of compounds of such high molecular weight. Although formula (II) has a high degree of probability, it is greatly to be desired that its validity should be further tested by the synthesis of neocyanine or by experiments on its breakdown.

EXPERIMENTAL.

Neocyanine Ethiodide.—Lepidine ethiodide (5 g.; 2 mols.), dry pyridine (20 c.c.), and ethyl orthoformate (5·5 g.; 4 mols.) were boiled together for 3 hours, during which crystals separated. These were collected when cold (0·89 g.; 21% yield) and recrystallised from spirit (1000 c.c.); the yield of neocyanine ethiodide (0·72 g.) was 17%. To isolate 1 : 1′-diethyl-4 : 4′-carbocyanine iodide, the pyridine mother-liquor was poured into boiling water, cooled, and

filtered. The solid obtained (2·23 g.; 56% yield) was recrystallised from spirit (150 c.c.) and resulted in 42% yield (1·67 g.). It was dried in a vacuum at 100—120° and analysed by the method of Carius, which methods of drying and analysis were used throughout this work (Found: I, 26·4. Calc. for $C_{25}H_{25}N_2I$: I, 26·4%).

According to the second method of preparing neocyanine ethiodide, lepidine (5·6 g.; 2 mols.) and ethyl *p*-toluenesulphonate (7·83 g.; 2 mols.) were heated at 140—150° for 3 hours, and the quaternary salt so formed was boiled with pyridine (30 c.c.) and ethyl orthoformate (13 c.c.; 4 mols.) for 3 hours. The hot reaction liquid, which was free from solid, was poured into an excess of boiling aqueous potassium iodide. The iodide obtained (5·9 g.) was boiled with successive quantities of spirit (50 c.c. × 6) until the filtrate was pure green, and the residue was then recrystallised from spirit (3000 c.c.): a 26% yield of neocyanine ethiodide (2·62 g.) resulted. The first two spirit solutions gave a 9% yield of crude 1 : 1′-diethyl-4 : 4′-carbocyanine iodide, which on recrystallisation from spirit (25 c.c.) gave a 7% yield (0·65 g.) (Found: I, 26·6%); the next four spirit solutions gave only a small amount of solid (0·03 g.), which was a mixture of the two dyes. That the neocyanine was completely freed from kryptocyanine was evident.

The large proportion of neocyanine ethiodide, as compared with 1 : 1′-diethyl-4 : 4′-carbocyanine iodide, afforded by the second method can hardly be attributable to the difference in the lepidine quaternary salt, and the separation of neocyanine ethiodide during the first reaction might be expected to favour its formation. In the following two comparative experiments, volumes of pyridine in the ratio 1 : 50 were taken: the dyes (1·08 g. and 0·81 g., respectively) obtained by the reaction of the quaternary salt from lepidine (1 c.c.; 2 mols.) and ethyl *p*-toluenesulphonate (1·50 g.; 2 mols.) with ethyl orthoformate (2·5 c.c.; 4 mols.) and pyridine (2 c.c. and 100 c.c., respectively) were boiled with successive quantities of spirit (each of 20 c.c.) and, when a green filtrate was obtained, the residue was recrystallised from spirit. In the case of the dye prepared in the solution of small volume the yield of recrystallised kryptocyanine was small compared with that of neocyanine (0·02 g.: 0·31 g.), whereas with more pyridine, the yield of kryptocyanine was large compared with that of neocyanine (0·30 g.: 0·08 g.).

When heated, 1 : 1′-diethyl-4 : 4′-carbocyanine iodide gives rise at about 205° to a tar of metallic appearance; sudden and violent decomposition occurs at about 260°, the exact point depending upon the rate of heating. Mills and Braunholtz (*loc. cit.*) give m. p. 253—254°.

Neocyanine ethiodide, unlike 1 : 1′-diethyl-4 : 4′-carbocyanine

iodide, only forms minute crystals, which show a coppery lustre, and it is also obtained in the form of a dull green powder. It is only very slightly soluble in spirit. It melts with decomposition at about 284° (Found : C, 57·25, 57·0 ; H, 5·1, 4·9 ; N, 5·1, 5·2 ; I, 32·2, 32·0. $C_{37}H_{37}N_3I_2$ requires C, 57·1 ; H, 4·8 ; N, 5·4 ; I, 32·7%).

Neocyanine Ethobromide.—The quaternary salt from lepidine (12·8 g. ; 2 mols.) and ethyl *p*-toluenesulphonate (17·9 g. ; 2 mols.) was boiled with pyridine (45 c.c.) and ethyl orthoformate (30 c.c. ; 4 mols.) for 3 hours, and the reaction mixture was poured into a hot solution of sodium bromide (18·5 g. in 100 c.c. of water). The resultant bromide (11·6 g.) was boiled with successive quantities of spirit (50 c.c. × 3), and the residue was then recrystallised from spirit (1500 c.c.) : the yield of neocyanine ethobromide (7·12 g.) was 35% of that theoretically possible. The first spirit solution gave a 5% yield (0·83 g.) of product which was chiefly 1 : 1′-diethyl-4 : 4′-carbocyanine bromide, m. p. about 250° (decomp.), and the second and third solutions gave a 2% yield (0·37 g.) of neocyanine.

In another experiment (2·04 g. of lepidine taken), in which 50 times the above proportion of pyridine was used, most of the solvent was distilled off after the condensation, and the residue was treated with sodium bromide. The crude bromide (2·35 g.) was boiled with spirit (20 c.c. × 2) : the first spirit solution gave a 52% yield (1·62 g.) of dye which was mainly 1 : 1′-diethyl-4 : 4′-carbocyanine bromide, the second gave a 4% yield (0·12 g.) of neocyanine ethobromide, and the undissolved residue (0·05 g.) amounted to a further 1% yield of neocyanine.

Neocyanine ethobromide forms small green and gold crystals and is considerably more soluble in spirit than is the corresponding ethiodide. It melts with decomposition at about 291° (Found : C, 64·2, 64·2 ; H, 5·6, 5·6 ; N, 5·9 ; Br, 23·2, 23·1. $C_{37}H_{37}N_3Br_2$ requires C, 65·0 ; H, 5·5 ; N, 6·15 ; Br, 23·4%).

Condensation of Lepidine Methiodide with Ethyl Orthoformate.—During the boiling of lepidine methiodide (3 g.) with pyridine (30 c.c.) and ethyl orthoformate (3½ c.c.) for 3 hours, much solid separated. It was collected when cold, and the yield of green crystals (1·44—1·80 g.) was 61—76%. In one experiment, boiling with successive quantities of spirit (100—200 c.c.), insufficient to dissolve all the solid, showed this to consist of 4 : 4′-carbocyanine free from neocyanine methiodide. In another case, recrystallisation from spirit (950 c.c.) gave a 37% yield (0·89 g.) of minute green crystals of 1 : 1′-dimethyl-4 : 4′-carbocyanine iodide (Found : I, 28·0. Calc. for $C_{23}H_{21}N_2I$: I, 28·1%).

Neocyanine Methobromide.—Lepidine (5·4 g. ; 2 mols.) and methyl *p*-toluenesulphonate (7·03 g. ; 2 mols.) were heated at 140—150°

for 3 hours and the resulting quaternary salt was boiled with pyridine (70 c.c.) and ethyl orthoformate (12½ c.c.; 4 mols.) for 3 hours, during which time much solid separated. This sulphonate was filtered off when cold, dissolved in a hot mixture of spirit (100 c.c.) and water (180 c.c.), and treated with aqueous sodium bromide (10 g. in 20 c.c. of water). The resulting bromide was washed and dried (5·6 g.). It was boiled with two lots of spirit (each of 100 c.c.) and, as the second filtrate was green, the residue was recrystallised from spirit (1100 c.c.): the resulting yield of neocyanine methobromide (3·13 g.) was 39%. The solid (0·29 g.) from the second spirit extract gave a green solution, so it was again crystallised from spirit (100 c.c.), and the further amount of neocyanine methobromide obtained (0·17 g.) brought the total yield up to 41%. The crystals (1·12 g.) from the first spirit extract consisted of a 22% yield of crude 1 : 1′-dimethyl-4 : 4′-carbocyanine bromide, and after recrystallisation from spirit (50 c.c.), the yield (0·72 g.) was 14%. The difference in solubility between this 4 : 4′-carbocyanine and the corresponding neocyanine is not so marked as in other cases, so that 1 : 1′-dimethyl-4 : 4′-carbocyanine bromide was not obtained free from the latter dye (Found: Br, 20·3. $C_{23}H_{21}N_2Br$ requires Br, 19·7%). The 4 : 4′-carbocyanine begins to decompose at about 265° and melting with violent decomposition occurs at about 275°. Neocyanine methobromide forms beautiful little crystals of a bright copper colour and these melt with decomposition at about 288° (Found: C, 64·0, 64·0; H, 5·1, 5·0; N, 6·1; Br, 24·5, 24·6. $C_{34}H_{31}N_3Br_2$ requires C, 63·6; H, 4·9; N, 6·55; Br, 24·9%). All three neocyanines show a very similar sensitising action.

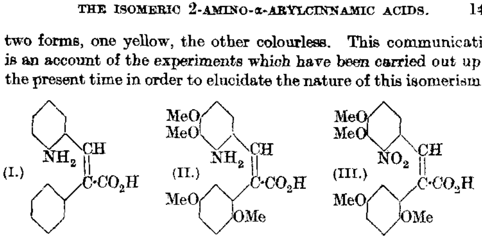
RESEARCH LABORATORY, ILFORD, LIMITED,
ILFORD, E. [*Received, April 4th, 1928.*]

CXCV.—*The Isomeric 2-Amino-α-arylcinnamic Acids.*

By JOHN MASSON GULLAND and CYRIL JOSEPH VIRDEN.

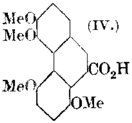
PSCHORR (*Ber.*, 1896, **29**, 496) observed that 2-amino-α-phenylcinnamic acid (I) exists in two interconvertible isomeric forms, one yellow, the other colourless. Stoermer and Prigge (*Annalen*, 1915, **409**, 23) confirmed this observation, but did not examine the isomerides more closely, and other workers who have prepared 2-amino-α-arylcinnamic acids make no mention of such isomerism. During an investigation into the constitution of thebenine (this vol., p. 921), we had occasion to prepare 2-amino-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamic acid (II), and found that it occurs in

two forms, one yellow, the other colourless. This communication is an account of the experiments which have been carried out up to the present time in order to elucidate the nature of this isomerism.

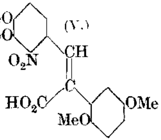


The synthesis of the amino-acids (II) follows the usual stages. 2 : 5-Dimethoxybenzaldehyde, prepared by introducing the aldehydo-group into *p*-dimethoxybenzene, condenses with hippuric acid, yielding the azlactone, 5-*keto*-2-*phenyl*-4-(2′ : 5′-*dimethoxybenzylidene*)-4 : 5-*dihydro-oxazole*, which is converted into α-*benzamido*-2 : 5-*dimethoxycinnamic acid* by heating for a short time with dilute hydrochloric acid or sodium hydroxide. Prolonged alkaline hydrolysis of the azlactone yields 2 : 5-*dimethoxyphenylpyruvic acid*, which is oxidised by hydrogen peroxide to 2 : 5-dimethoxyphenylacetic acid. When the sodium salt of this acid is condensed with 2-nitroveratraldehyde (Pisovschi, *Ber.*, 1910, **43**, 2137), trans-2-*nitro*-3 : 4 : 2′ : 5′-*tetramethoxy*-α-*phenylcinnamic acid* (III) is formed, together with a small amount of 2-nitro-3 : 4-dimethoxycinnamic acid (this vol., p. 931). The reduction of the acid (III) with ferrous sulphate and ammonia yields a mixture of two 2-*amino*-3 : 4 : 2′ : 5′-*tetramethoxy*-α-*phenylcinnamic acids* (II), A, m. p. 219°, which is colourless, and B, m. p. 167°, which is yellow; the marked difference of solubility in alcohol provides an easy method of separation. These acids are interconvertible: the addition of an excess of sodium acetate to a solution of either in dilute hydrochloric acid precipitates the acid B, and either acid, uncontaminated by the other, may readily be obtained at will when an ammoniacal solution of A or B is treated with acetic acid under conditions which are described in the experimental section. Both these acids must have the *trans*-configuration for the following reasons. In the first place, both yield 3 : 4 : 5 : 8-*tetramethoxyphenanthrene*-9-*carboxylic acid* (IV) when a methyl-alcoholic solution of the diazonium sulphate is boiled. When the acid (IV) is heated with glacial acetic acid in a sealed tube, it loses carbon dioxide and forms 3 : 4 : 5 : 8-*tetramethoxyphenanthrene*. Secondly, the corresponding *cis*-amino-acid exists only in alkaline solution. Thus, *trans*-2-nitro-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamic acid (III) is partly converted into

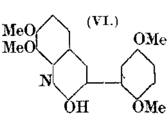
cis-2-nitro-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamic acid (V) when an aqueous solution of its sodium salt is exposed to ultra-violet light, and the reduction of the barium salt of this acid (V) with ferrous sulphate yields a solution from which hydrochloric acid precipitates 7 : 8 : 2′ : *5′-tetramethoxy-3-phenylcarbostyril* (VI) (compare Stoermer, *loc. cit.*, p. 18). The same carbostyril derivative is formed from the amino-acids (II), either by exposing an alcoholic solution of B to ultra-violet light, or by heating A or B with acetic anhydride and a trace of sulphuric acid.



(IV.)



(V.)



(VI.)

The difference in colour of alcoholic solutions of the acids A (almost colourless) and B (bright yellow) indicates that the isomerism is not due merely to dimorphism, and the molecular weights of the acids confirm this deduction. The acid B, m. p. 167°, proved to be unimolecular in camphor (Rast, *Ber.*, 1922, **55**, 1051), as was to be expected from its lower melting point and the close resemblance of its properties to those of other 2-amino-α-arylcinnamic acids. The acid A, m. p. 219°, on the other hand, was bimolecular, and therefore it became important to determine the molecular weights in other solvents, and to ascertain the effect of adding a small amount of one form to a saturated solution of the other (compare Sidgwick, J., 1915, **107**, 672). The sparing solubility of the acid A restricted the choice of solvent : in benzene, for example, it is practically insoluble. In azobenzene, the acids A and B were associated, but at comparable concentrations the observed values for the molecular weights of A were approximately twice those of B. In acetic acid, the acids A and B were readily soluble and both appeared to be unimolecular ; the values for A were consistently low, but it should be noted that this acid retains moisture, which cannot be eliminated without causing decomposition.

In acid or alkaline solutions the unimolecular form of the 2-amino-α-arylcinnamic acids predominates. (The properties of the hydrochloride and chloroplatinate of Pschorr's colourless amino-acid, *loc. cit.*, are also those of the corresponding derivatives of the yellow form, and we consider that these are all salts of the unimolecular yellow form.) In neutral solvents, on the other hand, the bi-

molecular is the stable form, and we have observed that in benzene or azobenzene the acid B changes into the acid A in a comparatively short time.

The precise nature of the bimolecular form of these acids can be elucidated only by the further study of this and other cases of the isomerism. Since the analytical data for Pschorr's acid indicate that it is anhydrous, it is not possible on the basis of the available evidence to decide whether the water of crystallisation of the acid A is essential for the production of the bimolecular form, or whether the A type is composed intrinsically of two molecules of the B type, and we wish therefore to record the facts, and to postpone the discussion of the theoretical question until a later publication.

Experimental.

2 : 5 - *Dimethoxybenzaldehyde.*—After several unsatisfactory attempts to introduce the aldebydo-group into quinol by the method of Tiemann and Müller (*Ber.*, 1881, **14**, 1986), the modification of the Gattermann aldehyde synthesis recommended by Adams and Levine (*J. Amer. Chem. Soc.*, 1923, **45**, 2373; 1924, **46**, 1518) was found to be satisfactory. The conditions which have already been detailed (this vol., p. 929) were closely adhered to, and the pure aldehyde was obtained in a yield of 70% of that theoretically possible.

5 - *Keto* - 2 - *phenyl* - 4 - (2′ : 5′ - *dimethoxybenzylidene*) - 4 : 5 - *dihydro - oxazole.*—This azlactone is obtained by heating together on a boiling water-bath 2 : 5-dimethoxybenzaldehyde (10 g.), hippuric acid (12 g.), fused sodium acetate (12 g.), and acetic anhydride (20 c.c.). The orange product is washed with cold alcohol and repeatedly boiled with water (yield, 75%); further treatment is unnecessary for the next stage. The *azlactone* crystallises from acetic acid, ethyl acetate, or ethyl alcohol, from which it separates in orange needles, m. p. 170—172° (Found: N, 4·4. $C_{18}H_{15}O_4N$ requires N, 4·5%).

α-*Benzamido*-2 : 5-*dimethoxycinnamic Acid*,

$C_6H_3(OMe)_2\cdot CH{:}C(NHBz)\cdot CO_2H$.

—When the azlactone is boiled for a short time with alcoholic hydrochloric acid or with dilute sodium hydroxide, a clear solution is obtained which deposits this *acid* on cooling or acidification, respectively. It separates from alcohol in colourless needles, m. p. 195—196° (Found in material dried at 100°: N, 4·5. $C_{18}H_{17}O_5N$ requires N, 4·3%). The azlactone is regenerated by boiling with acetic anhydride.

2 : 5-*Dimethoxyphenylpyruvic acid*, $C_6H_3(MeO)_2\cdot CH_2\cdot CO\cdot CO_2H$, is

obtained in 76% yield when the azlactone is hydrolysed by boiling 10% sodium hydroxide solution for 12 hours, and the product is separated from benzoic acid by the sulphur dioxide method of Haworth, Perkin, and Rankin (J., 1924, **125**, 1686). It separates from glacial acetic acid in cream-coloured octahedra, m. p. 166—170° (decomp.), which are rather readily soluble in methyl alcohol or acetone, but sparingly soluble in benzene (Found: C, 58·8; H, 5·5. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·3%).

3-Hydroxy-2′ : 5′-dimethoxy-2-benzylquinoxaline.—2 : 5-Dimethoxyphenylpyruvic acid (2 g.) and *o*-phenylenediamine (1 g.) in ethyl alcohol (5 c.c.) are heated on the water-bath for a few minutes. On cooling, the clear solution deposits colourless needles, which after recrystallisation from ethyl alcohol melt at 179—180°, and retain half a molecule of alcohol when dried in a vacuum desiccator (Found: loss at 120°, 7·1; N, 8·8. $C_{17}H_{16}O_3N_2,\frac{1}{2}EtOH$ requires loss, 7·2; N, 8·8%).

2 : 5-Dimethoxyphenylacetic acid, $(MeO)_2C_6H_3{\cdot}CH_2{\cdot}CO_2H$, is obtained (yield, 80%) when a solution of 2 : 5-dimethoxyphenylpyruvic acid (5 g.) in ice-cold sodium hydroxide (35 c.c. of 2*N*) is oxidised by perhydrol (5·5 c.c. made up to 20 c.c.). Next day the pure acid is precipitated in colourless needles by dilute sulphuric acid. It crystallises from benzene in plates, m. p. 123°, which dissolve readily in alcohol, ether, and acetone (Found: C, 60·8; H, 6·0. Calc.: C, 61·2; H, 6·1%). Wolkow and Baumann (*Z. physiol. Chem.*, 1892, **15**, 214) give m. p. 124·5°. The *sodium* salt is prepared by evaporating to dryness a solution of the acid in the calculated amount of aqueous sodium carbonate.

Condensation of 2-Nitroveratraldehyde with 2 : 5-Dimethoxyphenylacetic Acid. trans-*2-Nitro-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamic Acid* (III) *and* trans-*2-Nitro-3 : 4-dimethoxycinnamic Acid.*—A mixture of sodium 2 : 5-dimethoxyphenylacetate (10 g.), 2-nitroveratraldehyde (Pisovschi, *Ber.*, 1910, **43**, 2137) (30 g.), and acetic anhydride (200 g.) is heated at 100° for 60 hours. Water is then added to destroy the acetic anhydride, and the residual oil is repeatedly extracted with small quantities of boiling dilute sodium carbonate solution. On cooling, the combined extracts deposit long silky needles of sodium *trans*-2-nitro-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamate. These are ground with concentrated hydrochloric acid; the *acid* obtained, after being washed and dried (13·5 g.), crystallises from ethyl alcohol in bright yellow, hexagonal plates, m. p. 204—205° (Found: C, 58·9; H, 4·9. $C_{19}H_{19}O_8N$ requires C, 58·6; H, 4·9%).

Acidification with concentrated hydrochloric acid of the alkaline mother-liquor from which the sodium salt has separated (above)

precipitates *trans*-2-nitro-3 : 4-dimethoxycinnamic acid (1·5 g.), which crystallises from ethyl alcohol in colourless needles, m. p. 229° with softening from 216°. There is no depression in the melting point of a mixture of this acid with the cinnamic acid obtained by the condensation of 2-nitroveratraldehyde and malonic acid (compare this vol., p. 932). The amount of this acid which is produced in the condensation described above increases rapidly with rise in temperature, and in earlier experiments it was observed that when the reaction took place at 140° equal weights of the two acids were produced.

The Isomeric trans-2-*Amino*-3 : 4 : 2′ : 5′-*tetramethoxy*-α-*phenylcinnamic Acids, A and B* (II).—A hot solution of *trans*-2-nitro-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamic acid (13·0 g.) in dilute ammonia (100 c.c.) is added carefully (frothing) to a hot reducing mixture previously prepared by the addition of ammonia (*d* 0·880; 120 c.c.) to a solution of ferrous sulphate (83·6 g.) in hot water (150 c.c.); the mixture is heated on the water-bath for 30 minutes. After the ferrosoferric oxide has been thoroughly washed with dilute ammonia, the combined filtrate and washings are cooled and just acidified with glacial acetic acid. The product separates as a gummy mass which rapidly crystallises; on recrystallisation from ethyl alcohol, the acid A (7·5 g.) separates in colourless needles. From the alcoholic mother-liquor, when evaporated to small bulk and cooled, the acid B is obtained as yellow needles (0·5 g.). The quantity of this acid increases, and the amount of A decreases correspondingly, if an excess of acetic acid is used in precipitating the product of the reduction.

The *acid B* is purified by dissolving it in cold, dilute hydrochloric acid (charcoal) and precipitating it by the addition of sodium acetate solution. After being washed with water and dried on porous tile, it crystallises from ethyl alcohol in yellow needles, m. p. 167° (Found in material heated at 100°: C, 62·6, 62·3; H, 5·6, 5·7; N, 3·8; OMe, 33·2. $C_{19}H_{21}O_6N$ requires C, 63·5; H, 5·9; N, 3·9; 4OMe, 34·5%). The somewhat low percentage of carbon indicates the retention of traces of moisture, which are lost only by heating to 140° (Loss at 140°: 0·6, 0·7%. Found in material dried at 140°: C, 63·5; H, 6·0%). The acid forms a yellow solution in dilute hydrochloric acid and a colourless solution in dilute sodium hydroxide or carbonate or ammonia, and is precipitated from these by the addition of sodium acetate or acetic acid respectively. It dissolves rather readily in methyl or ethyl alcohol, forming a bright yellow solution, but is sparingly soluble in cold benzene. It was converted into an uncrystallisable gum when a 0·1% aqueous solution was boiled under reflux for 12 hours.

When an ethyl-alcoholic solution of the acid B in a silica flask is exposed to ultra-violet light for several days, 7 : 8 : 2′ : 5′-tetramethoxy-3-phenylcarbostyril (VI) separates quantitatively as colourless needles, m. p. 189° (Found : C, 64·3; H, 5·7. $C_{19}H_{19}O_5N$ requires C, 64·6; H, 5·4%). The same substance is obtained by heating for 30 minutes on the water-bath a solution of the acid (0·5 g.) in acetic anhydride (5 c.c.) containing one drop of concentrated sulphuric acid, pouring the mixture into water, and crystallising the precipitate from alcohol. It is insoluble in sodium carbonate, but dissolves in concentrated sodium hydroxide or concentrated hydrochloric acid.

The *acid A*, when obtained as described above, softens at 180° and melts at 198°. In attempting to purify it in the first instance, it was dissolved in sodium bicarbonate and precipitated by the slow addition of glacial acetic acid and scratching. On this occasion only was the acid A reprecipitated in this way; in all subsequent cases, the acid B separated. Further investigation showed that the acid A *is obtained in a pure condition when a solution of* the crude acid, m. p. 198°, in dilute ammonia is just neutralised with the requisite quantity of acetic acid (previously determined by titration); no separation takes place until the vessel is scratched; the acid A is then precipitated as a colourless, crystalline powder. On recrystallisation from ethyl alcohol it forms colourless needles, m. p. 219°, which retain water of crystallisation at 140° (Found : C, 62·1, 62·3, 62·4; H, 6·2, 6·4, 6·2. $C_{19}H_{21}O_6N,\frac{1}{2}H_2O$ requires C, 62·0; H, 6·0%). It dissolves sparingly in hot ethyl alcohol, forming a faintly yellow solution from which it crystallises on cooling, and it is insoluble in benzene (mean f. p. of benzene, 0·061°; after addition of the acid A, 0·059°). Its solution in dilute hydrochloric acid is yellow, and in sodium hydroxide or carbonate or ammonia colourless; the addition of sodium acetate or acetic acid, respectively, precipitates the acid B. On the other hand, by neutralising a solution of either acid, A or B, in dilute ammonia by the sudden addition, with vigorous mechanical stirring, of the calculated amount of acetic acid (previously *determined*), *a clear, colourless solution is obtained which* deposits the acid A on scratching. This difference in the precipitation of the two acids is presumably due to the formation of a neutral, supersaturated solution, and explains the production of both acids in the reduction of the nitro-acid and careful precipitation by acetic acid. The acid A crystallised unchanged when a 0·1% aqueous solution which had been boiled under reflux for 12 hours was concentrated. When heated with acetic anhydride and sulphuric acid as described in the case of the acid B, it is converted quantitatively into 7 : 8 : 2′ : 5′-tetramethoxy-3-phenylcarbostyril (VI).

Molecular weights of the acids A and B. For $C_{19}H_{21}O_6N$, $M = 359$.

Acid.	Solvent.	% Concentration.	*M*.	Remarks.
B	Camphor.	10·0	357	Rast's method.
A		5·6	723	
		11·2	732	
B	Acetic acid.	0·6	328	
A		0·4—2·8	254	Mean of 6 results between 249 and 258.
B	Azobenzene.	2·0	623	
		5·2	839	
		8·8	1100	
A		1·4	1211	

Transformation of the Acid B into the Acid A in Azobenzene.—The azobenzene was distilled, crystallised from ethyl alcohol, and dried at 100°, and the samples of the acids were dissolved in the solvent by warming to about 80°, except where otherwise stated. The freezing point of a freshly prepared solution of the acid A, saturated at about 80°, was 0·211° below that of azobenzene, but it is probable that the solution was supersaturated, since the depression fell to 0·06° in the course of 1½ hours. The addition (without warming) of some of the acid B to the fresh solution of A increased the depression to 0·436°. The depression of a freshly prepared 8·8% solution of the acid B was 0·666°, and after ½ hour this had decreased to 0·229°. On addition of some of the acid A (without warming), the freezing point continued to rise (0·198°), and after ½ hour the depression was 0·088°. On dissolving the azobenzene in benzene, the whole of the amino-acid was recovered in the insoluble, bimolecular form.

cis-*2-Nitro-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamic Acid* (V) *and its Reduction.*—A concentrated aqueous solution of sodium *trans*-2-nitro-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamate in a quartz flask is exposed to ultra-violet light for 8 days. (Subsequent experiments showed that the yield of *cis*-acid is not increased by more prolonged exposure.) The solution is then just acidified with acetic acid, and the unchanged *trans*-acid (4·75 g.) which separates is removed. The addition of concentrated hydrochloric acid now precipitates the *cis*-acid (0·15 g.) in an impure condition. The combined yields of *cis*-acid from two experiments are recrystallised from ethyl alcohol, from which the *cis*-acid separates in pale yellow needles, m. p. 186° (Found : C, 58·4; H, 4·9. $C_{19}H_{21}O_8N$ requires C, 58·6; H, 4·9%).

The alkaline reduction of this acid yields a solution of the corresponding *cis*-2-amino-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamic acid, which passes into 7 : 8 : 2′ : 5′-tetramethoxy-3-phenylcarbostyril (VI) on acidification. A solution of the *cis*-nitro-acid (0·08 g.)

in a little dilute ammonia is added to a hot reducing mixture, prepared from barium hydroxide (0·55 g.) in hot water (10 c.c.) and ferrous sulphate (0·53 g.) in hot water (8 c.c.). During the reaction a stream of nitrogen is passed through the vessel in order to prevent atmospheric oxidation of the ferrous hydroxide. The mixture is heated on the water-bath for 15 minutes and filtered, and the cooled filtrate is acidified by hydrochloric acid. The carbostyril which separates crystallises from ethyl alcohol in colourless needles, m. p. 189°; there is no depression of the melting point of a mixture of this preparation with the material obtained from the *trans*-amino-acid.

3 : 4 : 5 : 8-*Tetramethoxyphenanthrene*-9-*carboxylic Acid* (IV).—An ice-cold solution of *trans*-2-amino-3 : 4 : 2′ : 5′-tetramethoxy-α-phenylcinnamic acid (4 g.) in methyl alcohol (60 c.c.) and sulphuric acid (40 c.c. of 2*N*) is diazotised, and the clear red solution is diluted with water and heated at 60° until the evolution of nitrogen ceases; the *acid* is then precipitated as a gum, which becomes crystalline on being rubbed with alcohol (yield, about 50%). The acid crystallises from ethyl alcohol in colourless needles of constant m. p. 190—198° (Found: C, 66·2; H, 5·2. $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%).

3 : 4 : 5 : 8-*Tetramethoxyphenanthrene*.—The preceding acid (1 g.) in glacial acetic acid (40 c.c.) is heated in a sealed tube at 240° for 40 hours. The dark solution is poured into water, made alkaline with ammonia, and extracted with ether. The extract is washed and dried, the solvent evaporated, and the residual oil crystallised repeatedly from methyl alcohol, from which 3 : 4 : 5 : 8-*tetramethoxyphenanthrene* separates in light brown needles, m. p. 118—120° (Found: C, 71·9; H, 5·9. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·0%).

The *picrate*, prepared in alcoholic solution, separates from ethyl alcohol in dark chocolate needles, m. p. 158° (Found: N, 7·9. $C_{24}H_{21}O_{11}N_3$ requires N, 7·9%).

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CXCVI.—*The Action of Bromine Water on Certain Olefinic Hydrocarbons and Ethers.*

By JOHN READ and WILLIAM GALLOWAY REID.

FROM the series of researches indicated in a recent communication (this vol., p. 745), it has become evident that wide use may be made of chlorine water and bromine water as reagents for the addition of hypochlorous and hypobromous acids to olefinic substances. The present paper describes the application of bromine water in this way to styrene and a number of related aromatic ethers, and also to amylene and *dl*-Δ^3-menthene. Since the first-named group yields bromohydrins which are not readily affected by hot water, it has been possible to adduce four further examples in which the yield of bromohydrin is increased by raising the temperature during the reaction with bromine water. Under the conditions adopted, the percentage yields of bromohydrin obtained at the ordinary temperature and at about 90°, respectively, were as follows: styrene, 77·9, 96·7; anethole, 47·9, 76·1; safrole, 65·2, 69·2; *iso*safrole, 67·0, 72·8. Taking into account the behaviour of oleic acid and indene (*loc. cit.*), it thus appears to be a general rule that when the halogenohydrin is stable towards hot water the ratio halogenohydrin/dihalogenide increases with rise of temperature. The yield of halogenohydrin is increased also by dilution. At concentrations from about 0·1 to 0·2 gram-molecule per litre, yields of more than 90% of the amounts of bromohydrin theoretically possible have now been obtained by the action of bromine water on the following substances: ethylene, sodium maleate, sodium fumarate, itaconic acid, indene, styrene, cinnamic acid, methylcoumaric acid, and methylcoumarinic acid. Of the other substances investigated, maleic acid and allyl alcohol gave yields of more than 85%; and amylene, anethole, safrole and *iso*safrole gave from about 70% to 80%, *dl*-Δ^3-menthene 62·9%, and oleic acid 51·5%.

It has already been pointed out that the reactions in question may be used, *inter alia*, for the rapid and convenient preparation of aldehydes and ketones from olefinic substances, *e.g.*, of phenylacetaldehyde from cinnamic acid, and of β-hydrindone from indene (J., 1921, **119**, 1775; 1922, **121**, 2551); we describe below a similar conversion of amylene (trimethylethylene) into trimethylethylene oxide and methyl *iso*propyl ketone. We have also taken occasion to prepare certain αβ-amino-alcohols by the action of cold concentrated ammonia on the corresponding bromohydrins. Thus, styrene yields β-hydroxy-β-phenylethylamine; since the same base has been obtained by reducing *iso*nitrosoacetophenone (Kolshorn,

Ber., 1904, **37**, 2483), the position of the amino-group and the mode of addition of the hypobromous acid are thereby established. In a similar way, we have prepared β-hydroxy-β-*p*-methoxyphenyl*iso*propylamine (m. p. 84°) from anethole, and have moreover resolved it into optically active components (m. p. 80—81°). β-Hydroxy-α-*p*-methoxyphenylpropylamine has been described by Takeda and Kuroda (*J. Pharm. Japan*, 1919, 561); our substance appears to be identical with an isomeric alkamine (m. p. 80°), of undetermined constitution, prepared by these authors. By applying the same method to amylene we have been able to prepare γ-amino-β-hydroxy-β-methylbutane, an asymmetrically constituted base which we have as yet been unable to submit to optical resolution.

Experimental.

The Action of Bromine Water on Styrene.—(1) To 500 c.c. of water, maintained at about 90°, were added four successive portions of 5 g. of styrene. To the mixture, thoroughly emulsified in each instance by vigorous shaking, a 7% solution of bromine in aqueous potassium bromide (10%) was added with moderate rapidity until the attainment, after continued shaking, of a permanent yellow tint. The amount of bromine added at each stage was noted, and its distribution was determined by titrating the resulting hydrobromic acid in a small measured volume of the aqueous solution with standard sodium bicarbonate.

The proportion of bromine converted into bromohydrin and hydrobromic acid declined in the successive stages from 97·6% to 94·9%, and of the total amount of bromine added (25·85 g.), 96·7% reacted in this way, leaving only 3·3% to function in the formation of dibromide. From these results it is also apparent that of the 20 g. of styrene used, only 16·8 g. reacted, owing possibly to the presence of polymerisation products.* Extraction with ether yielded a limpid, amber-coloured liquid (35 g.), having $n_D^{17°}$ 1·5780. The bulk of the product (21 g.), distilling at 109—110°/2 mm., and having $n_D^{17°}$ 1·5800, $d_{4°}^{20°}$ 1·4994, consisted of styrene bromohydrin, or β-*hydroxy*-β-*phenylethyl bromide*, OH·CHPh·CH_2Br. This substance is a heavy, colourless liquid, with an irritating odour; it is almost insoluble in water (Found: Br, 40·0. C_8H_9OBr requires Br, 39·8%). It was impracticable to distil the product of the reaction at 10 mm., owing to decomposition.

(2) Upon conducting the operation at the ordinary temperature, the yield of bromohydrin fell to 77·9%, and the extracted oily product deposited crystals of styrene dibromide (αβ-dibromo-α-phenyl-

* The original styrene distilled completely between 78° and 85°, and 80% passed over between 80° and 83°.

ethane) when kept (m. p. 74—75°) (Found: Br, 60·1. Calc. for $C_8H_8Br_2$: Br, 60·4%). Attempts to prepare the bromohydrin from the dibromide by digestion with aqueous alcohol or acetone in presence of calcium carbonate were unsuccessful, the dibromide remaining practically unaltered after 10 hours. It is thus improbable that the enhanced yield of bromohydrin at the higher temperature is due to partial hydrolysis of the dibromide.

β-*Hydroxy*-β-*phenylethylamine*, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}NH_2$.—Styrene bromohydrin (10 g.) was shaken mechanically with concentrated aqueous ammonia (50 g.) for 10 hours. The excess of ammonia was then removed by spontaneous evaporation in an open dish, and the oily by-products (including bromostyrene) by subsequent extraction with ether. The concentrated aqueous residue yielded a brownish-yellow syrup (1·7 g.) when basified with potassium hydroxide and extracted with ether. This product consisted of the free hydroxy-amine, and when submitted to the Schotten-Baumann reaction with benzoyl chloride it readily gave the corresponding benzoyl derivative, m. p. 143° (*Ber.*, 1904, **37**, 2483) (Found: C, 74·2; H, 6·5. Calc. for $C_{15}H_{15}O_2N$: C, 74·7; H, 6·2%).

The Action of Bromine Water on Anethole.—(1) To 10 g. of anethole emulsified in 250 c.c. of water at about 90° was gradually added bromine (10·85 g.; 1 mol.) dissolved in aqueous potassium bromide (10 g. in 150 c.c.), the mixture being shaken vigorously throughout the process. A determination of the resulting hydrobromic acid showed that 76·1% of the bromine had reacted to form this substance and the bromohydrin. The pasty product, when extracted with ether and dried (17 g.), deposited crystals of anethole dibromide (m. p. 67°). The residual viscid syrup, which had a very irritating odour, decomposed when heated in a vacuum apparatus.

(2) When the operation was repeated at the ordinary temperature, a suspension of finely powdered anethole in water being used, only 47·9% of the bromine reacted to form bromohydrin and hydrobromic acid, and a larger proportion of crystalline anethole dibromide was isolated from the product. In both instances the calculated quantity of bromine reacted with the anethole.

β-*Hydroxy*-β-p-*methoxyphenyl*iso*propylamine*,

$$MeO{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CHMe{\cdot}NH_2.$$

—Anethole bromohydrin (50 g.), prepared from anethole dibromide (*Ber.*, 1905, **38**, 3470), was shaken for 3 days with concentrated ammonia (250 g.). After the product had been exposed over-night in an open dish, the residual oil was extracted with ether; the aqueous washings of the ethereal extract were added to the original aqueous liquor, and most of the water was removed by evaporation on the water-bath. The free base, isolated in the usual way, formed

a viscid syrup (7 g.), which gradually crystallised; the colourless product obtained by washing with ether melted at 84°. The base is insoluble in light petroleum, moderately easily soluble in ether, and readily soluble in water. The *hydrochloride*, after recrystallisation from acetone, melted at 182°; it is very soluble in alcohol or water (Found: Cl, 16·3. $C_{10}H_{15}O_2N,HCl$ requires Cl, 16·3%). The *benzoyl* derivative crystallised from alcohol in fine needles, m. p. 159°; the *benzylidene* derivative is a viscid syrup.

The crude *d*-camphorsulphonate had $[\alpha]_D$ +15·0°, $[M]_D$ +62°, in 1% aqueous solution. After two fractional recrystallisations from hot absolute alcohol, this salt yielded large colourless prisms of d-β-*hydroxy*-β-p-*methoxyphenyl*iso*propylamine* d-*camphorsulphonate*, m. p. 194—195°, $[\alpha]_D$ +20·5°, $[M]_D$ +85°; the rotatory power was unaltered by further recrystallisation. d-β-*Hydroxy*-β-p-*methoxyphenyl*iso*propylamine* separates from ether in needles, m. p. 80—81°. The following determinations of optical rotatory power were made at 15°: $[\alpha]_D$ +4·6°, $[M]_D$ +8° (water, *c* 1·0); $[\alpha]_D$ +13·9°, $[M]_D$ +25° (methyl alcohol, *c* 1·0); $[\alpha]_D$ +18·4°, $[M]_D$ +33° (ethyl alcohol, *c* 0·6); $[\alpha]_D$ +22·9°, $[M]_D$ +41·5° (benzene, *c* 1·2); $[\alpha]_D$ +21·7°, $[M]_D$ +39° (acetone, *c* 0·6). The *hydrochloride*, m.p. 171—172°, had $[\alpha]_D$ +14·7°, $[M]_D$ +32°, in water (*c* 0·9) (Found: Cl, 16·3%). The *benzoyl* derivative crystallised from alcohol in fine needles, m. p. 153—154°; a 0·5% alcoholic solution showed no measurable optical activity when examined in a 2-dcm. tube in sodium light.

The crude *d*-α-*bromocamphorsulphonate* of the inactive base formed large prisms, m. p. 103°.

The Action of Bromine Water on Safrole.—A procedure was adopted exactly similar to that described for anethole. At about 90°, 69·2% of the added bromine was used in the formation of bromohydrin and hydrobromic acid, and at the ordinary temperature the proportion fell to 65·2%. In both instances the calculated amount of bromine was absorbed, and 10 g. of safrole yielded 17 g. of a dark brown, viscid syrup with an irritating odour; when kept for a while, this deposited colourless needles of *safrole dibromide*, which melted at 87° after being collected and washed with ether (Found: Br, 49·1. $C_{10}H_{10}O_2Br_2$ requires Br, 49·7%). The dibromide obtained by brominating safrole in chloroform and other organic solvents was a liquid which could not be induced to crystallise.

The Action of Bromine Water on iso*Safrole, Eugenol, and* iso-*Eugenol.*—*iso*Safrole behaved very similarly to safrole, the proportions of bromine functioning in the formation of bromohydrin and hydrobromic acid being 72·8% at 90° and 67·0% at the ordinary temperature.

Upon treating *isos*afrole bromohydrin (50 g.; compare *Ber.*,

1905, **38**, 3469) with concentrated ammonia, in the way described for styrene bromohydrin, it yielded a viscid oil (6 g.), which appeared to consist of β-*amino-α-hydroxydihydro*iso*safrole*,

$CH_2O_2{:}C_6H_3{\cdot}CH(OH){\cdot}CHMe{\cdot}NH_2$.

The *hydrochloride* separated from acetone in colourless needles, m. p. 154° (Found: Cl, 15·2. $C_{10}H_{13}O_3N,HCl$ requires Cl, 15·3%).

Eugenol and *iso*eugenol yielded indefinite tarry products when treated with bromine water, even when the mixtures were cooled in ice-water; this result is probably to be associated with the phenolic character of these ethers.

The Action of Bromine Water on Amylene.—The commercial amylene used in this work consisted mainly of trimethylethylene (b. p. 37°); 10% distilled below 34°, 77% between 34° and 40°, and 8% between 40° and 50°. The crude amylene (10 g.) was emulsified with water (200 c.c.) at the ordinary temperature and treated gradually, in the usual way, with a solution of bromine (22·9 g.; 1 mol.) in water (300 c.c.) containing dissolved potassium bromide (20 g.). A permanent yellow tinge was produced after the addition of 73·3% (220 c.c.) of this solution; so that 26·7% of the hydrocarbon mixture appeared to be unaffected by bromine water. Titration disclosed that 78·9% of the added bromine had reacted to form bromohydrin and hydrobromic acid. The product was isolated, by extraction with ether, as a limpid, pale yellow liquid (18 g.) with an irritating odour. After three successive fractional distillations under diminished pressure, this material gave a 50% yield of a colourless liquid which distilled completely at 45—46°/12 mm. and appeared to be identical with the amylene bromohydrin (γ-bromo-β-hydroxy-β-methylbutane) prepared by Mokiewsky (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 900) (Found: Br, 48·1. Calc. for $C_5H_{11}OBr$: Br, 47·9%).

γ-*Amino-β-hydroxy-β-methylbutane*, $OH{\cdot}CMe_2{\cdot}CHMe{\cdot}NH_2$.—Upon shaking amylene bromohydrin (40 g.), prepared as above, for 24 hours in a stoppered bottle with concentrated ammonia (200 g.) the oily layer gradually diminished but did not disappear completely. Excess of ammonia was allowed to evaporate in an open dish, and the oil was extracted with ether; when recovered, it had $n_D^{18°}$ 1·5043 and contained no bromohydrin or base. The aqueous layer, when evaporated to small bulk, basified, and extracted with ether, yielded a brown oil (11·5 g.) with a strong basic odour; the bulk of this product distilled at 60—62°/16 mm. as a pale yellow oil. The *chloroplatinate* separated from a strong aqueous solution in orange prisms, m. p. 186° (decomp.) [Found: Pt, 31·8. $(C_5H_{13}ON)_2,H_2PtCl_6$ requires Pt, 31·7%]. The *benzoyl* derivative was obtained as an oil, and the p-*nitrobenzoyl* derivative melted

indefinitely at about 65°. The d-*α-bromocamphorsulphonate* crystallised from acetone in felted masses of colourless needles, m. p. 170°; systematic fractional crystallisation from this solvent yielded fractions with values of $[\alpha]_D$ ranging from +61° to +66° in dilute aqueous solution, but no appreciable optical rotation was discernible in dilute alcoholic solutions of specimens of the free base regenerated from such fractions. The d-*camphorsulphonate* separated from ethyl acetate in glistening plates, m. p. 144°; fractional crystallisation of this salt also failed to yield an indication of the optical resolution of the base.

Trimethylethylene Oxide (βγ-oxy-β-methylbutane), $Me_2C\overset{O}{—}CHMe$.—Upon heating amylene bromohydrin with potassium hydroxide dissolved in methyl or ethyl alcohol, it proved impracticable to separate the resulting trimethylethylene oxide from the solvent. Accordingly, the bromohydrin (200 g.) was added to potassium hydroxide (70 g.) dissolved in water (500 c.c.), the mixture being heated for ½ hour on the water-bath under reflux, with frequent shaking. After the upper oily layer had been separated, the aqueous liquid was distilled until no more oil passed over; upon adding the distillate to the oily layer, drying the mixture with sodium sulphate, and distilling it, the whole (53 g.) passed over at 74—78°. From this result, taken in conjunction with the observed values $d_4^{20^\circ}$ 0·8277, $d_4^{0^\circ}$ 0·8288, and $n_D^{18^\circ}$ 1·3896, the product appeared to be identical with trimethylethylene oxide described by Eltekow (*J. Russ. Phys. Chem. Soc.*, 1882, **14**, 361).

Methyl iso*Propyl Ketone*, $CHMe_2{\cdot}COMe$.—Heat was evolved upon adding trimethylethylene oxide to dilute sulphuric acid, and the product which was isolated after the mixture had been boiled for 2 hours under reflux consisted of a mixture of methyl *iso*propyl ketone and the corresponding glycol. The ketone was prepared in better yield (10 g.) by heating amylene bromohydrin (25 g.) with litharge (50 g.) and lead chloride (10 g.) at 200° for 7 hours in a sealed tube; it was also formed by heating the bromohydrin with water at 100° (compare *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 287).

The Action of Bromine Water on dl-*Δ^3-Menthene.*—We are indebted to Dr. G. J. Robertson, of this College, for the particulars of a method devised by him for preparing *dl*-Δ^3-menthene (compare Milobedzki and Kolitowska, *Roczniki Chem.*, 1926, **6**, 67):

dl-Menthol (31·2 g.) was added gradually to phosphorus trichloride (27·5 g.; 1 mol.), the container being cooled in water. The clear liquid was then heated slowly to 80° and kept at that temperature for about an hour, until the evolution of hydrogen chloride had practically ceased. The product was poured into ice-water, and the

oil was extracted with ether, washed with water, and dried over sodium sulphate. After two fractional distillations under diminished pressure, *dl*-Δ^3-menthene,* b. p. 60—62°/15 mm., was obtained in good yield (23 g.).

dl-Δ^3-Menthene (10 g.), emulsified with ice-water (250 g.) by vigorous shaking in a stout glass bottle, was treated gradually in the usual way with bromine (11·6 g.; 1 mol.) dissolved in an aqueous solution (150 c.c.) of potassium bromide (10 g.). The bromine was decolorised at once, and the calculated amount was readily absorbed; 62·9% was found by titration to have reacted in the formation of hydrobromic acid and bromohydrin. The product was isolated by extraction with ether as an amber-coloured oil (16 g.), having $n_D^{15°}$ 1·5111; it decomposed when submitted to vacuum distillation (Found: Br, 42·6. A mixture of 62·9% $C_{10}H_{19}OBr$ and 37·1% $C_{10}H_{18}Br_2$ requires Br, 42·5%). The utilisation of this product as a source of substances of interest in the chemistry of terpenes is under investigation.

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CXCVII.—*Optical Activity and the Polarity of Substituent Groups. Part IX. Menthyl Esters of Methoxynaphthoic and of Diphenyl-2-carboxylic Acids.*

By EGON BRETSCHER, H. GORDON RULE, and JOHN SPENCE.

IN earlier communications of this series emphasis has been placed on the influence of *o*, *p*-directive substituents in lowering the molecular rotation, when introduced into the *o*-position in an optically active ester of benzoic acid. In continuance of this line of investigation, the examination of a number of menthyl esters of methoxynaphthoic acids has now been undertaken, the methoxyl group having been selected as the substituent owing to the exceptionally large depression produced by this group in the rotatory powers of menthyl and *sec.*-β-octyl benzoates.

The *a*- and β-naphthoic acids, in comparison with benzoic acid, offer the advantage of several different *o*-positions. Moreover, the *peri*-compounds of the naphthoic series have many points in common with the *o*-derivatives, and it appeared probable that an examination

* *l*-Menthol, when treated similarly, was found by Dr. Robertson to yield a partly racemised *d*-Δ^3-menthene, having $[a]_D^{15°}$ +22·3°.

of compounds of this type might be of assistance in determining whether the peculiar *o*-effect in question is transmitted through the chain of carbon atoms or through space.

Very little information is so far available regarding the influence of substituents on the rotatory powers of active naphthoic esters. The unsubstituted menthyl 1- and 2-naphthoates have been investigated by Rupe (*Annalen*, 1903, **327**, 186), the rotatory power of menthyl 1-methoxy-2-naphthoate in the crude state was measured by Cohen and Dudley (*J.*, 1910, **97**, 1748), and that of the 3-methoxy-2-naphthoate * by these authors and by Pickard and Kenyon (*J.*, 1915, **107**, 58). In the present work, the menthyl esters of 2-, 4-, 5-, and 8-methoxy-1-naphthoic acids have been prepared and examined, and the preparations of the unsubstituted 1-naphthoate and of the 1- and 3-methoxy-2-naphthoates have been repeated, the 1-methoxy-derivative having now been obtained in the optically pure state. In addition, the menthyl esters of diphenyl-2-carboxylic acid and of 2′-methoxydiphenyl-2-carboxylic acid have been prepared for the purpose of comparison.

An interesting and hitherto unrecorded feature of the crystalline 3-methoxy-2-naphthoic ester and of the newly prepared 8-methoxy-1-naphthoate is the powerful triboluminescence they exhibit. This was first observed on crushing a cake of the 3 : 2-derivative in a mortar in bright daylight. The deep violet flashes emitted were plainly visible and resembled a strong electric discharge. The 5-methoxy-ester also is triboluminescent, but the remaining crystalline esters, the 4 : 1- and the 2 : 1-compounds, do not possess this property.

Values of $[M]_D$ obtained for the various menthyl esters, together with other values recorded in the literature, are summarised in Tables I and II. Molecular rotatory powers of the esters of diphenyl-2-carboxylic acid and of 2′-methoxydiphenyl-2-carboxylic acid in solution are given in Table III. Among the crystalline esters, only the 3-methoxy-2-naphthoate could be maintained in the supercooled condition. The 2-, 4-, 5- and 8-methoxy-1-naphthoates melted at comparatively high temperatures and solidified a few degrees below these points; the rotatory powers of these esters were therefore determined in solution.

* There is some confusion in the literature regarding these acids. 1-Methoxy-2-naphthoic acid, described by Cohen and Dudley as *α*-methoxynaphthoic acid, is listed in Stelzner's Literaturregister (1910—11, p. 705) as 4-methoxy-1-naphthoic acid. Similarly, the 3 : 2-acid, described as *β*-methoxynaphthoic acid, is listed as the 2 : 1-compound. The uncertainty is possibly due to the authors tabulating the ester of the *α*-acid under the heading of *p*-compounds, and that of the *β*-acid under *o*-compounds (p. 1735), and is increased by the fact that the melting points quoted for both acids are too low.

TABLE I.

Menthyl 1-Naphthoates.

Substit.	Solvent.	c.	$[M]_D^{20^\circ}$.
None	$CHCl_3$	4·990	−222° [3]
,,	$C_2H_5\cdot OH$	9·090	−245·9 [1]
,,	C_6H_6	4·938	−273 [3]
2-MeO	C_6H_6	5·000	+ 20·7
,,	C_6H_6	20·00	+ 34·0
4-MeO	C_6H_6	5·000	−313·4
,,	$CHCl_3$	5·000	−250
5-MeO	C_6H_6	4·642	−262·9
,,	$CHCl_3$	4·663	−231
8-MeO	C_6H_6	4·987	−129·6
,,	$C_2H_5\cdot OH$	4·995	−155·6
,,	CS_2	4·972	−114·9

TABLE II.

Menthyl 2-Naphthoates.

Substit.	Solvent.	c.	$[M]_D^{20^\circ}$.
None	C_6H_6	11·11	−287·6° [2]
1-MeO	Homog.	—	−223·8 [4]
3-MeO	Homog. (100°)	—	−164·5 [5]
,,	$CHCl_3$	5·017	−123
,,	C_6H_6	5·000	−174 [6]
,,	CS_2	5·000	−159·5 [6]

[1] Rupe, *Annalen*, 1910, **373**, 121. [2] Tschugaeff, C., 1902, II, 1238. [3] See the experimental section of this paper. [4] Cohen and Dudley, *loc. cit.*, record $[M]_D = -239°$ for the crude ester. [5] Cohen and Dudley find $[M]_D = -166·4°$. [6] Kenyon and Pickard, *J.*, 1915, **107**, 58.

TABLE III.

Menthyl Diphenyl-2-carboxylate and 2′-Methoxydiphenyl-2-carboxylate.

Unsubstituted ester.	Substituted ester.
In C_6H_6 (c = 5·194) $[M]_D^{20^\circ}$ = −201°.	In C_6H_6 (c = 5·63) $[M]_D^{20^\circ}$ = −323°.
	In $C_2H_5\cdot OH$ (c = 5·37) $[M]_D^{20^\circ}$ = −302°.

TABLE IV.

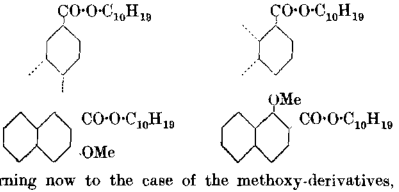
Molecular Rotations $[M]_D$ of Aromatic Esters [7] at 20°.

Active alcohol.	Solvent.	Benzoate.	1-Naphthoate.	2-Naphthoate.
Menthol	C_6H_6	—	−273° [9]	−287·6° [8]
,, ...	$C_2H_5\cdot OH$	−234·1°	−246	—
d-β-Octanol	$C_2H_5\cdot OH$	+ 91·9	+ 53·7	+129·4
d-γ-Nonanol	$C_2H_5\cdot OH$	+ 29·8	− 8·0	+ 68·4
d-Benzylmethylcarbinol	$C_2H_5\cdot OH$	+169·1	+104·5	+371·1

[7] Kenyon and Pickard, *loc. cit.*, p. 115. [8] Tschugaeff, *loc. cit.* [9] This paper.

Influence of Substitution on Rotatory Power.—Before discussing the specific influence of the methoxyl group, it is instructive to compare the rotatory powers of 1- and 2-naphthoic esters with those of the corresponding benzoates. Reference to Table IV, which summarises the molecular rotatory powers recorded in the literature for the esters of menthol, *d*-β-octanol, *d*-γ-nonanol and *d*-benzylmethylcarbinol, shows that the substitution of the 2-naphthoyl group for the benzoyl group results in every case in a marked increase in the rotation. This increase cannot be due merely to the presence of the second unsaturated nucleus, since the rotatory powers of the

1-naphthoates are in general actually lower than those of the corresponding benzoates. All these differences, however, may be correlated with the changes in rotatory power following nuclear substitution in *sec.*-β-octyl benzoate and other active derivatives of benzene. In such compounds *m*-substituents tend to raise the rotatory power and *p*-substituents to bring about a still greater increase, whether the substituent be *o*, *p*- or *m*-directive in type.* Now the change from a benzoic ester to one of 2-naphthoic acid is equivalent to a 3 : 4-substitution in the benzene nucleus and thus is accompanied by an increase in rotatory power. On the other hand, the passage from the 2-naphthoic to the 1-naphthoic ester corresponds to the transference of a ring junction from the *p*- to the *o*-position with respect to the carboxylic complex. As the substituent is here of the *o*, *p*-directive type (leading to the formation of α-derivatives in naphthalene), the change results in a reduction of rotatory power, owing to the characteristic influence of such groups in the *o*-position.



Returning now to the case of the methoxy-derivatives, it has *previously been demonstrated that a methoxyl group in the* *o*-position depresses the rotatory power of menthyl benzoate (Cohen and Dudley, *loc. cit.*) and of *sec.*-β-octyl benzoate, whereas in the *p*-position it raises the value. The same regularity is now found to hold for the menthyl methoxynaphthoates (Tables I and II).

The simplest example is that of the 2-naphthoic ester, in which the *o*-substituent may occupy either of the positions 1 and 3. It will be observed that the depression in rotatory power is more

* This generalisation holds for the substituents NO_2, Cl, $CH_3{\cdot}O$, CO_2H, and CH_3, when introduced into the nucleus in octyl benzoate (Rule, Hay, Numbers, and Paterson, this vol., p. 178). Similar changes occur in the nuclear-substituted methyl dibenzoyltartrates (Frankland, Carter, and Adams, J., 1912, **101**, 2470) and the substituted dianilides of tartaric acid (Frankland and Twiss, J., 1910, **97**, 155). The relation is also evident in the menthyl benzoates, although here the influence of *m*- or *p*-substitution on rotatory power is in some cases almost negligible (Cohen, J., 1914, **105**, 1892; 1918, **113**, 57).

pronounced in the case of the 3-methoxy-ester, which may be explained provisionally on the assumption of a screening effect exercised by the substituent. Each of the side chains attached to the ring bearing the carboxyl group has its own specific influence on the rotation, and following the generalisation formulated above it would be expected that the union of the second ring would depress the rotatory power in the *o*-position, but raise it to an increasing extent as it passes from the *m*- to the *p*-position. In menthyl 3-methoxy-2-naphthoate the elevating influence of the *p*-ring junction on the active complex appears to be partially screened by the substituents in the intermediate positions. The chief influences at work here are the depressive effect of the *o*-methoxy-group and the comparatively small elevating effect of the *m*-ring junction. In 1-methoxy-2-naphthoate the *m*-ring junction appears to be screened, whilst the stronger elevating influence of the *p*-junction has full play, thus leading to a higher rotatory power for this isomeride than for the 3-methoxy-derivative.

Among the menthyl 1-naphthoates, a methoxyl group in the 2-position exerts so marked an influence that the rotatory power is actually reversed in sign. This is a rare phenomenon with *l*-menthyl esters; a similar dextrorotation has also been recorded for menthyl triphenylacetate (Tschugaeff, *Ber.*, 1912, **45**, 2760), menthyl 1 : 4-dihydronaphthoate (Rupe, *Annalen*, 1903, **327**, 186), and certain complex thio-esters (Tschugaeff, *Ber.*, 1909, **42**, 2246). In the present instance the reversal appears to be due to the additive lowering influence of two groups, each of the *o*, *p*-directive type. The case is thus analogous to that of the 2 : 6-dibromobenzoic ester examined by Cohen (J., 1914, **105**, 1892), in which the combined effect of the two bromine atoms in the *o*-positions, although insufficient to reverse the sign of the rotation, reduces the value of $[M]_D$ from $-233°$ to $-19°$.

A special interest attaches to the 8-methoxy-1-naphthoate, in which the substituent also leads to a marked diminution in rotatory power. The resemblance between *peri*- and *o*-compounds as revealed in their chemical behaviour (*e.g.*, anhydride formation and steric hindrance) is therefore also evident in the optical activity of these compounds. This similarity lends further support to the view that the peculiar effect of *o*-substituents on the rotatory power of aromatic esters is transmitted through space and not through the carbon chain (compare also Rule, Hay, and Paul, this vol., p. 1347).

On the other hand, a comparison of the rotatory powers in benzene solution shows that when the methoxyl is introduced into the *p*-position with respect to the carboxyl group, as in the 4-methoxy-1-

naphthoate, it raises the value. In the 5-position, however, the substituent produces no observable change.

The derivatives of diphenylcarboxylic acid were prepared in order to discover whether the presence of a methoxyl substituent in the ortho-position to the common bond joining the two nuclei led to a depression in rotatory power as in the *peri*-compound of naphthalene. This was found not to be the case. In benzene solution the menthyl 2′-methoxydiphenyl-2-carboxylate ($[M]_D$ −323°) has a higher rotation than the unsubstituted ester ($[M]_D$ −201°). The influence of the methoxyl group in this case appears to be of the *general polar* type as in the acetic esters and in the *p*-substituted benzoic esters (compare Rule, Hay, Numbers, and Paterson, *loc. cit.*). This is readily understood in view of the comparatively free rotation of the two nuclei round the bond joining them, and of other observations relating to diphenyl compounds. Robinson (J., 1927, 2488), for example, comments on the fact that 2′ : 2-dinitrodiphenyl is inactive towards alcoholic ammonia at 150°. Burton and Kenner (J., 1922, **121**, 495) and Le Fèvre and Turner (this vol., p. 247) conclude that the two nuclei are independent systems joined by a bond which is not a link in a true conjugated system. In the *peri*- and *o*-derivatives the methoxyl group is maintained permanently in close proximity to the asymmetric complex. A comparison of the two diphenylcarboxylic esters with menthyl benzoate ($[M]_D$ −239°) is interesting. The introduction of the phenyl group into the *o*-position in the benzoate does not lead to an increase in rotatory power, as might have been anticipated from its cyclic and unsaturated character, but has the usual depressive effect of an *o*, *p*-directive grouping in this position.

Influence of Solvents.—The values recorded in Tables I and I[illegible] show that the character of the solvent affects the rotatory powers o[illegible] the naphthoic esters to a greater extent than those of the corre[illegible]sponding benzoic esters. In the case of menthyl 2-methoxy-1[illegible] naphthoate, the rotation is negative in chloroform and aceton[illegible] but positive in benzene and in concentrated solutions in carbo[illegible] disulphide. In each solvent examined, the rotatory power [illegible] this ester becomes increasingly positive with increasing concen[illegible]tration, thus indicating that the homogeneous ester has a com[illegible]paratively high positive rotation. The highest positive rotation[illegible] were observed in benzene ($c = 20$ and $c = 5$) and in carbon di[illegible]sulphide ($c = 34$).

Dispersion.—With the exception of menthyl 2-methoxy-1[illegible] naphthoate, the above methoxynaphthoic esters proved to hav[illegible] normal dispersion under the conditions of experiment. Whe[illegible] $1/\alpha$ is plotted against λ^2, it is found that the deviations from th[illegible]

linear, although very small, are systematic rather than casual. The dispersion of these compounds may therefore be described as normal and complex. The dispersion ratios, $\alpha_{4358}/\alpha_{5893}$, for the 1-naphthoates vary between 2·06 and 2·17. The 3-methoxy-2-naphthoate gives considerably lower ratios, varying from 1·95 in the homogeneous state to the surprisingly low valne of 1·54 in chloroform solution.

Menthyl 2-methoxy-1-naphthoate exhibits a dispersion which is complex and under certain conditions anomalous. When the values obtained for this compound at various concentrations in different solvents are plotted in the form of a characteristic diagram (Armstrong and Walker, *Proc. Roy. Soc.*, 1913, *A*, **88**, 388), the points all lie on the diagram with the exception of those for the rotatory powers of 30% and 40% solutions in chloroform. Anomalous dispersion is observed in chloroform, $c = 40$, and in carbon disulphide, $c = 5$.

During the preparation of the menthyl ester of diphenyl-2-carboxylic acid by way of the acid chloride, it was found that under certain conditions a considerable proportion of fluorenone was formed. This point is being further investigated.

EXPERIMENTAL.

The menthol employed in the following preparations was specially purified and had $[\alpha]_D^{20^\circ} = -49{\cdot}75^\circ$ in alcohol, $c = 10$.

Menthyl 2-*Methoxy*-1-*naphthoate*.—The required methoxy-acid was obtained by a modification of Bodroux's method (*Compt. rend.*, 1903, **136**, 617). Magnesium, activated with iodine, was brought into reaction with 1-bromo-2-methoxynaphthalene, and the cooled ethereal suspension of the finely divided magnesium compound was treated with solid carbon dioxide at −40°. The crnde acid was dissolved in the minimum amount of alkali and dilute mineral acid was added drop by drop with vigorous shaking, a gummy impurity being precipitated. As soon as the methoxy-acid hegan to deposit as a white powder the liquid was filtered and acidified. After twice crystallising from alcohol, the methoxy-acid was pure, m. p. 176°. The yield was 63%. Bodroux obtained less than 20%, largely owing to his method of purification.

2-Methoxy-1-naphthoyl chloride, prepared by means of thionyl chloride, was purified by *rapid* distillation under diminished pressure (yield, almost quantitative).

Menthyl 2-*methoxy*-1-*naphthoate* was obtained from the acid chloride (23 g.) and menthol (16 g.) dissolved in benzene (100 c.c.), with the gradual addition of pyridine (17 g.). The reaction is very vigorous and the mixture should be well cooled to prevent the

formation of coloured products. The ester separates from ligroin in long needles, m. p. 122—123° (Found: C, 77·5; H, 8·3. $C_{22}H_{28}O_3$ requires C, 77·6; H, 8·3%).

Menthyl 4-*Methoxy*-1-*naphthoate*.—4-Methoxy-1-naphthaldehyde (24 g.) was first prepared from α-naphthyl methyl ether (25 g.) and hydrogen cyanide by Gattermann's method (*Annalen*, 1907, **357**, 366). The aldehyde, in an equal weight of pyridine, was diluted with hot water, and the emulsion shaken until cold. Oxidation with potassium permanganate then gave the acid in 78% yield.

4-Methoxy-1-naphthoyl chloride, prepared by means of thionyl chloride, distilled at 210—215°/15 mm.

Menthyl 4-*methoxy*-1-*naphthoate* was obtained from the acid chloride and menthol, dissolved in a small amount of chloroform, pyridine being used as condensing agent. The ester was crystallised from ligroin until of constant rotatory power. M. p. 114—115° (Found: C, 77·4; H, 8·5. $C_{22}H_{28}O_3$ requires C, 77·6; H, 8·3%).

Menthyl 8-*Methoxy*-1-*naphthoate*.—1 : 8-Naphtholactone (Eckstrand, *J. pr. Chem.*, 1888, **38**, 159, 278) (8·5 g.), dissolved in *N*-aqueous sodium hydroxide (110 c.c.), was cooled with ice and mechanically shaken while methyl sulphate (28 g.) was added in four portions during ½ hour, and after 1 hour's shaking the product was heated at 100° to destroy any excess of the methylating agent. *Methyl* 8-*methoxy*-1-*naphthoate* was removed from the alkaline mixture by extraction with ether. It separated from light petroleum in colourless, rhombic plates, m. p. 51—52° (Found: C, 72·1; H, 5·7. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%). 8-*Methoxy*-1-*naphthoic acid*, together with some unchanged hydroxy-acid, remained in the alkaline liquid. Addition of diazotised sulphanilic acid converted the hydroxy-acid into a dye. After 3 hours, the methoxy-acid and the dye were precipitated by means of hydrochloric acid as a viscous mass which soon solidified. This was dried on tile over phosphoric oxide and extracted with benzene, leaving the dye as a dark red powder. The methoxy-acid separates from benzene in glistening needles, which lose their lustre on standing. M. p. 162—163° (corr.) (Found: C, 71·2; H, 5·3. $C_{12}H_{10}O_3$ requires C, 71·2; H, 5·0%).

Two separate methylations of 8·5 g. of the naphtholactone were carried out with sodium hydroxide as alkali, and two others with potassium hydroxide in the same proportion and concentration. The former gave a total of 9·5 g. of ester and 11·7 g. of acid; the latter gave 15·0 g. of ester and 6·3 g. of acid.

Menthyl 8-*methoxy*-1-*naphthoate* could not be prepared by way of the acid chloride, as the reaction with thionyl chloride did not

proceed smoothly and led to resinification. The methoxy-acid (12 g.) and menthol (36 g.) were heated for 42 hours at 120°, a few bubbles of hydrogen chloride being passed through the mixture at intervals. The mixture was worked up in the usual way and gave the ester as an oil (6·4 g.) which solidified on standing. On distillation under 0·09 mm. pressure it was obtained colourless. The ester separated from light petroleum in colourless prisms, m. p. 96—96·5° (Found: C, 77·3; H, 8·5. $C_{22}H_{28}O_3$ requires C, 77·6; H, 8·3%). After two crystallisations from light petroleum the rotatory power remained constant. Some of the ester was hydrolysed; the liberated menthol was unchanged in optical rotation.

Menthyl 1-*Methoxy*-2-*naphthoate*.—Cohen and Dudley (*loc. cit.*) give 120—123° as the m. p. of the free acid, whereas Hübner (*Monatsh.*, 1894, **15**, 735) records 127°. For these and other reasons the preparation was repeated, but methyl sulphate was used in place of the iodide. A test methylation was carried out with aqueous alkali in the usual manner, but titration of the resulting acid with a standardised solution of benzenediazonium chloride (Fierz, "Farbenchemie," p. 245) showed that 63% of the hydroxy-acid had escaped reaction. Methylation of the dry disodium salt for 6 hours in boiling xylene was more successful. After the product had been washed with alkali and distilled under diminished pressure, an oil, b. p. 174—178°/15 mm., was obtained which, on hydrolysis with alcoholic alkali and subsequent acidification, gave an acid containing only 28% of the hydroxy-compound; the latter was removed by treatment with diazotised sulphanilic acid. The methoxy-acid crystallised from benzene in needles, m. p. 126—127°.

The crude menthyl 1-methoxy-2-naphthoate obtained from this acid had a rotatory power somewhat higher than that of the pure ester. The viscous oil was distilled under 0·02 mm. pressure, the main fraction boiling at 172—174°. Two further fractionations failed to alter the rotatory power of $[M]_D^{100°}$ −224° (Cohen and Dudley record $[M]_D^{100°}$ = −239° for the crude ester).

Menthyl 3-methoxy-2-naphthoate was prepared from a methoxy-acid which melted at 133—134° (compare Lesser, Kranepuhl, and Gad, *Ber.*, 1925, **58**, 2120; Fries and Schimmelschmidt, *ibid.*, p. 2838). Its rotatory power agreed with that previously found by Cohen and Dudley.

Menthyl 5-*Methoxy*-1-*naphthoate*.—Laurent's acid was converted into 5-methoxy-1-naphthoic acid by the method of Royle and Schedler (J., 1923, **123**, 1641) and Shoesmith and Rubli (J., 1926, 3241). Unchanged hydroxy-acid was removed by treatment with diazotised sulphanilic acid and the purified methoxy-acid (m. p.

229°) was esterified in the usual manner. The *menthyl* ester crystallises from methyl alcohol in colourless, glistening plates, m. p. 90·3°. It is readily soluble in ligroin, benzene and chloroform, but is less soluble in alcohol or light petroleum (Found : C, 77·8; H, 8·4. $C_{22}H_{28}O_3$ requires C, 77·6; H, 8·3%).

Menthyl Diphenyl-2-carboxylate..—Diphenyl-2-carboxylic acid was prepared from fluorenone by fusion with potash. The purified and colourless acid (m. p. 110—111°) was carefully brought into reaction with thionyl chloride. The resulting acid chloride was treated with menthol, and the heating continued for 2 hours at 40°. The reaction mixture was extracted with ether, the extract washed with alkali, and the ether distilled off. Menthol was removed by distillation in steam. The resulting viscous oil was almost colourless and distilled at 175°/0·4 mm. Fractionation was repeated until no further change in rotatory power was observed (Found : C, 82·0; H, 8·4. $C_{23}H_{28}O_2$ requires C, 82·1; H, 8·4%).

Under more vigorous treatment, the acid chloride underwent partial ring closure to yield fluorenone (see also Rule and Bretscher, *J.*, 1927, 925). The above sample of ester, however, gave no reaction with *p*-nitrophenylhydrazine, a reagent with which it is possible to detect the presence of very small amounts of the ketone.

Menthyl 2'-methoxydiphenyl-2-carboxylate could not be prepared by way of the acid chloride (Rule and Bretscher, *loc. cit.*), but was obtained from the free acid by esterification at 120° in the presence of hydrogen chloride. After 30 hours' heating, 11 g. of acid and 33 g. of menthol gave 7·1 g. of crude ester, $[\alpha]_D = -85·5°$ in benzene ($c = 5$). On distillation under 0·3 mm. pressure the ester came over at 171—173°. Fractionation was repeated twice more, after which the rotatory power was $[\alpha]_D = -82·3°$. It is possible that this value might have undergone a further small change on continued fractionation, but the quantity was insufficient for this to be carried out (Found : C, 78·3; H, 8·2. $C_{24}H_{30}O_3$ requires C, 78·6; H, 8·3%).

Menthyl 1-naphthoate prepared from purified naphthoic acid had the same rotatory power as previously found by Tschugaeff (*loc. cit.*).

Rotations in the Homogeneous State.

t.	*d.*	*l.*	$[M]_{6708}$.	$[M]_{5893}$.	$[M]_{5461}$.	$[M]_{4358}$.	$\alpha_{4358}/\alpha_{5893}$.
			Menthyl 1-methoxy-2-naphthoate.				
98°	1·0267	0·5	−166·5°	−223·8°	−267·8°	−488·9°	2·18
			Menthyl 3-methoxy-2-naphthoate.				
20	1·083	0·5	—	−164·5	−193·5	−320·4	1·95
98	1·025	0·5	—	−164·7	−181·1	−297·0	1·85

Rotations in Solution at about 20° (l = 2).

Solvent.	c.	$[M]_{6708}$.	$[M]_{5893}$.	$[M]_{5461}$.	$[M]_{4358}$.	$\alpha_{4358}/\alpha_{5893}$.
			Menthyl 1-naphthoate.			
$C_2H_5 \cdot OH$...	8·991	—	−247°	—	—	—
C_6H_6	4·938	−201°	−273	−319°	−560°	2·05
$CHCl_3$	4·990	−172	−222	−266	−451	2·02
			Menthyl 2-methoxy-1-naphthoate.			
C_6H_6	5·000	+ 10·8	+ 20·7	+ 28·9	+ 92·5	4·46
C_6H_6	20·00	+ 21·9	+ 34·0	+ 45·3	+121	3·55
CS_2	5·000	− 16·3	− 19·4	− 16·3	+ 7·82	—
CS_2	34·00	—	+ 12·2	+ 20·6	+ 78·2	0·39
$COMe_2$ ...	5·00	− 45·8	− 55·9	− 62·2	− 78·8	1·40
$CHCl_3$	5·00	− 54·4	− 68·0	− 76·2	−105	1·54
$CHCl_3$	30·0	− 36·0	− 43·9	− 48·0	− 49·1	1·12
$CHCl_3$	40·0	− 27·7	− 33·0	− 39·9	− 22·4	0·68
			Menthyl 4-methoxy-1-naphthoate.			
C_6H_6	4·994	—	−313	−374	−667	2·13
$CHCl_3$	4·999	−190	−250	−302	−514	2·06
			Menthyl 5-methoxy-1-naphthoate.			
C_6H_6	4·642	−198·6	−263	−325	−563	2·14
$CHCl_3$	4·663	−182	−231	−287	—	—
			Menthyl 8-methoxy-1-naphthoate.			
$C_2H_5 \cdot OH$...	5·000	−116·1	−156	−184·5	−326·5	2·10
C_6H_6	4·987	− 97·5	−130	−157	−282	2·17
CS_2	4·972	− 87·2	−115	−137·5	−242	2·11
			Menthyl 3-methoxy-2-naphthoate.			
$CHCl_3$	5·017	—	−123	−139	−190	1·54
			Menthyl diphenyl-2-carboxylate.			
C_6H_6	5·194	−151	−201	−233	—	—
			Menthyl 2′-methoxydiphenyl-2-carboxylate.			
C_6H_6	5·630	−245	−323	−390	−692	2·14
$C_2H_5 \cdot OH$...	5·370	−223	−302	−362	−654	2·17

Summary.

The influence of the typically *o*-, *p*-directive methoxyl group on the rotatory powers of the menthyl naphthoates has been examined and found similar to that exerted in the case of menthyl benzoate.

1. In any position adjacent to the carboxylic complex the substituent depresses the rotatory powers of the 1- and 2-naphthoates. In menthyl 2-methoxy-1-naphthoate the combined effect of the two *o*-, *p*-directive groups in the 2- and 6-positions actually reverses the sign of the rotation, giving a dextrorotatory ester.

2. In 4-methoxy-1-naphthoate the *p*-substituent raises the rotation, but in the 5-position it has little or no effect.

3. A methoxyl group in the *peri*-position also produces a marked diminution in rotatory power, thus indicating that the peculiar

o-influence in question is transmitted through space and not through the chain of atoms.

4. A phenyl group in the 2-position in menthyl benzoate leads to the diminished rotation characteristic of *o*-, *p*-directive substituents. A 2-methoxyphenyl group in this position raises the rotation.

5. The relative magnitudes of the rotatory powers of optically active esters of benzoic acid, 1-naphthoic acid, and 2-naphthoic acid may be correlated with the known influence of *o*-, *m*-, and *p*-substituents on the benzoic esters.

The authors desire to express their gratitude to the Earl of Moray Fund for a grant which has covered most of the expense of this investigation.

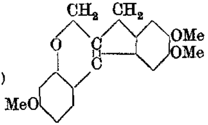
UNIVERSITY OF EDINBURGH. [*Received, April 25th, 1928.*]

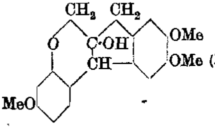
CXCVIII.—*Experiments on the Synthesis of Brazilin and Hæmatoxylin and their Derivatives. Part III.**

By WILLIAM HENRY PERKIN, jun., JNANENDRA NATH RÂY, and ROBERT ROBINSON.

THE synthesis of deoxytrimethylbrazilone (I) (anhydrotrimethylbrazilin) was described in Part II of this investigation (J., 1927, 2094) and it was not anticipated that the conversion of this substance into *O*-trimethylbrazilin (II) would offer any considerable difficulty.

(I.)





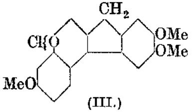
(II.)

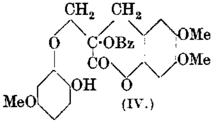
* This communication was written up for publication before the appearance of a paper by Pfeiffer, Angern, Haack, and Willems (*Ber.*, 1928, **61**, 839) dealing in part with a similar subject matter.

In view of this repeated duplication of research, we have thought it well to indicate clearly our projected lines of investigation. In the hæmatoxylin series, we prefer to publish our experiments in a more complete form; they have already reached the stage now disclosed in connexion with brazilin. We have, however, employed throughout protection of the hydroxyl groups by ethylene radicals in the place of methyl groups. Hence the substances we have made are different from those described by Pfeiffer and his collaborators and therefore there does not appear to be any necessity to hurry publication, no novel theoretical point being involved in the passage from the brazilin to the hæmatoxylin series.

Actually the problem has proved to be a very puzzling one, chiefly on account of the remarkable properties of deoxytrimethylbrazilone (I). This substance is prone to undergo oxidation; when merely shaken with pyridine and aqueous sodium hydroxide a considerable proportion of the material becomes alkali-soluble in a short time, and in the presence of acids there is a strong tendency to form the *iso*brazilein salt.

When, for example, a stream of dry hydrogen chloride was led through a solution of deoxytrimethylbrazilone in cold chloroform, with ordinary precautions to exclude air, an orange crystalline substance was gradually deposited consisting of *iso*brazilein hydrochloride trimethyl ether (III).


(III.)


(IV.)

Many other attempts to add the elements of water or of an acid, HX, to deoxytrimethylbrazilone were unsuccessful.

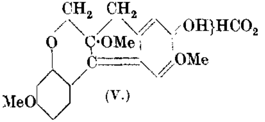
Oxidation of deoxytrimethylbrazilone with perbenzoic acid in chloroform solution gave various products under different conditions. The procedure described in the experimental section leads to the production of a *substance* to which we ascribe the formula (IV) largely by analogy with the products derived from brazilein derivatives by oxidation with hydrogen peroxide (Engels, Perkin, and Robinson, J., 1907, **91**, 1175).

In other experiments along these lines we obtained evidence that an oxygen atom may be inserted between the central carbon atom of the diphenylmethane structure and the pyrocatechol nucleus, because a crystalline oxidation product of deoxytrimethylbrazilone (1 mol.) with perbenzoic acid (1·5 mols.) was found to be converted, by gentle warming with sulphuric acid, into a pyrylium salt exhibiting the characteristic pink colour in acid solution and the phenomenal greenish-yellow fluorescence of methoxychromenodimethoxybenzopyrylium salts (Part I, J., 1926, 950). This oxidation product was quite homogeneous and had m. p. 123°, but unfortunately we have not succeeded in reproducing the conditions for its preparation. In none of these experiments, however, was there any indication that deoxytrimethylbrazilone could be transformed into an oxide of the ethylene oxide type.

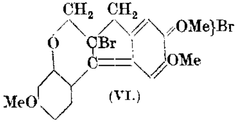
The deep crimson dibromide of deoxytrimethylbrazilone closely resembles the compounds of trimethylbrazilein and tetramethyl-

dihydrobrazileinol with acids and unquestionably all these substances are analogous to the salts derived from *o*- and *p*-methoxytriphenylcarbinols and to the rosaniline salts. The characteristic trimethylbrazilein formate, therefore, may he formulated as (V). Here the representation of one nucleus in the full quinonoid condition is adopted for purposes of convenience only; doubtless the kationic charge will be distributed in part to the oxygen atoms of the resorcinol nucleus, and even in part to the central carbon atom, and both nuclei will be partly quinonoid.

The corresponding formula for deoxytrimethylbrazilone dibromide is (VI).



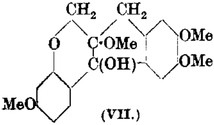
(V.)



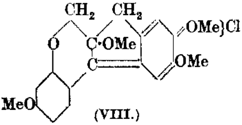
(VI.)

The action of zinc dust on (VI) in acetic acid suspension and solution leads to the formation of deoxytrimethylbrazilone and thus it is clear that the double bond of this substance is closely conjugated with the aromatic nuclei. All attempts to reduce the unsaturated quinonoid centres, leaving the centrally-situated bromine atom intact, were fruitless.

The analogy existing between (V) and (VI) is well brought out by the observation that the reduction of trimethylbrazilein by means of zinc dust in the presence of hot acetic and hydrochloric acids yielded a phenolic product and on methylation with metbyl sulphate and sodium hydroxide this was transformed into deoxytrimethylbrazilone. Furthermore the reduction of tetramethyldihydrobrazileinol (VII) under similar conditions gave deoxytrimethylbrazilone. It is clear that the anhydro-hydrochloride of tetramethyldihydrobrazileinol (VIII) behaves as if it were the additive



(VII.)



(VIII.)

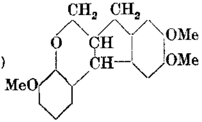
product, deoxytrimethylbrazilone–methyl hypochlorite. When the dibromide (VI) is treated in cold acetic acid suspension with potassium acetate a colourless, amorphous bromo-acetate is obtained. The acetoxy-group is doubtless attached to position 4 in the pyran

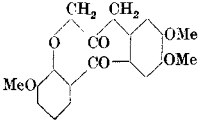
ring, but it was not found possible to replace the bromine atom by methoxyl and so achieve a synthesis of tetramethyldihydrobrazileinol (VII).

Preliminary experiments indicated that the bromo-acetate could be oxidised by chromic acid with formation of trimethylbrazilone. Another noteworthy property of deoxytrimethylbrazilone dibromide is the ease with which it loses hydrogen bromide with formation of *iso*brazilein hydrobromide trimethyl ether; this change occurs on keeping and very quickly in the presence of acetone.

On reduction with hydrogen and a palladium catalyst deoxytrimethylbrazilone furnishes a *dihydro*-derivative (IX) and this yields trimethylbrazilone (X) when it is oxidised by chromic acid in acetic acid solution. Thus trimethylbrazilone and its numerous derivatives have now been synthetically prepared and may be employed instead of deoxytrimethylbrazilone as starting points in attempted syntheses of *O*-trimethylbrazilin.

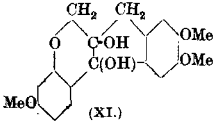
(IX.)



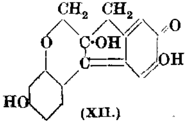


(X.)

From this point of view the reduction of trimethylbrazilone to the *pinacol* (XI) is of much interest and this change was accomplished by means of zinc dust in alcoholic acetic acid solution. The product exhibited the reactions expected of a trimethyldihydrobrazileinol, giving crystalline, crimson salts of the type (V) with acids and *iso*brazilein hydrogen sulphate trimethyl ether on gentle warming with sulphuric acid. Reduction of (XI) in strongly acid solution afforded deoxytrimethylbrazilone, and experiments on the reduction products obtained in neutral or alkaline media are still in progress.



(XI.)



(XII.)

It would be surprising if it does not prove feasible to pass from the pinacol (XI) to *O*-trimethylbrazilin. Nevertheless brazilin itself is the real ultimate object of these synthetical experiments and one of the methods we contemplate is the following:

(A) Demethylation of (IX), followed by acetylation or benzoylation of the trihydric phenol and oxidation to triacetylbrazilone or tribenzoylbrazilone.

(B) Preparation of triacetylbrazilone or tribenzoylbrazilone from acetylated or benzoylated brazilin (see p. 1513).

(C) Reduction of triacetylbrazilone or tribenzoylbrazilone to a pinacol.

(D) Hydrolysis of the pinacol and formation of *dl*-brazilein (XII).

(E) Reduction of brazilein to brazilin and resolution of *dl*-brazilein or *dl*-brazilin into the enantiomorphous forms.

The details require further elaboration and we wish to reserve for a short time the investigation of the processes involved in the above scheme and naturally in the analogous syntheses of tetra-acyl hæmatoxylone, hæmatein, and hæmatoxylin.

E X P E R I M E N T A L.

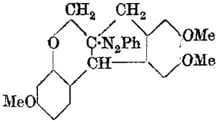
Preparation of Deoxytrimethylbrazilone.—The methylation of brazilin by means of methyl sulphate does not appear to have been described.

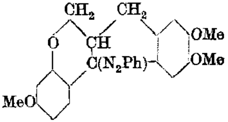
Potassium hydroxide (30 g.), dissolved in water (40 c.c.) and methyl alcohol (20 c.c.), was added to a solution of brazilin (40 g.) in hot methyl alcohol (100 c.c.), air being excluded by means of coal-gas. Methyl sulphate (50 g.) was then introduced gradually, the temperature not being allowed to rise above 50°. Further quantities of potassium hydroxide and of methyl sulphate equal to those already used were then introduced and finally the reaction was completed by heating the mixture at 65° for 15 minutes. The product was precipitated by water (800 c.c.), washed, and dried (yield, 42—45 g.). It may be employed without crystallisation for the preparation of trimethylbrazilone.

The reduction of trimethylbrazilone by means of phenylhydrazine (Gilhody and Perkin, J., 1902, **81**, 1046) does not proceed satisfactorily in ethyl-alcoholic solution, but the following method works well and we are inclined to suspect that it is the method originally used and that "alcohol" is a manuscript error (*loc. cit.*, p. 1047, line 3). Trimethylbrazilone (8 g.) was gradually added to a mixture of acetic acid (40 c.c.) and phenylhydrazine (25 c.c.) at 40° so that the temperature remained between 60° and 70°. The mixture was then heated at 80° for ½ hour, and the prodnct began to crystallise. After cooling, the solid was collected and washed with small quantities of acetic acid and then with alcohol (yield, 4—4·5 g.).

On keeping, the mother-liquor deposited a by-product, which crystallised from acetic acid in bright yellow needles, m. p. 245° (Found: C, 71·8; H, 5·5; N, 6·8. Calc. for $C_{25}H_{24}O_4N_2$: C, 71·7;

H, 5·7; N, 6·7%. Calc. for $C_{25}H_{22}O_4N_2$: C, 72·4; H, 5·3; N, 6·8%). The substance is evidently identical with a compound, $C_{25}H_{22}O_4N_2$, m. p. 239—242°, described by Herzig and Pollak (*Ber.*, 1905, **38**, 2166) as the main product of the action of phenylhydrazine on trimethylbrazilone in acetic acid solution. This substance may be a pyrazoline derivative as already suggested (Perkin and Robinson, J., 1908, **93**, 489), but one of the annexed formulæ is also possible.





There is evidence that a nitrogen atom is attached to the diphenylmethane carbon atom in that the substance is readily reduced by stannous chloride and hydrochloric acid, giving an eosin-red solution. This suggests the production of a diphenylcarbinol derivative in the reduction. The colourless reduction product, precipitated on the addition of water, is under examination. It dissolves in sulphuric acid to a deep green dichroic solution.

Attempts have been made to prepare deoxytrimethylbrazilone more directly from trimethylbrazilin by dehydration or equivalent processes. The action of phosphorus pentachloride on trimethylbrazilin in cold chloroform solution was energetic and on the addition of light petroleum a quantity of *iso*brazilein hydrochloride trimethyl ether was thrown down. The filtrate contained a gum that could not be crystallised; the substance was doubtless the chloride corresponding to trimethylbrazilin, but when it was heated with dimethylaniline there was no evidence of the formation of deoxytrimethylbrazilone.

Action of Perbenzoic Acid on Deoxytrimethylbrazilone.—An ice-cold solution of perbenzoic acid (1·38 g.) in chloroform (30 c.c.) was added to one of deoxytrimethylbrazilone (3·1 g.) in chloroform (30 c.c.), and the mixture kept at 0° for 4 hours. The solution was then washed with cold aqueous sodium carbonate (0·5 g. in 30 c.c.), dried, and evaporated in a vacuum. The residue dissolved in alcohol (10 c.c.) and on keeping in the ice-chest a voluminous crystalline mass separated. The *substance* (IV) crystallised from alcohol in transparent, rectangular plates, m. p. 152° (Found: C, 64·5; H, 5·2. $C_{26}H_{24}O_6$ requires C, 65·0; H, 5·0%). The substance is sparingly soluble in alcohol and although it is not attacked by aqueous sodium carbonate, it dissolves in aqueous sodium hydroxide.

Decomposition occurs on heating and benzoic acid can be isolated after acidification of the solution. The yellow solution in sulphuric acid becomes successively green, blue, purple and brownish-red on heating. The reaction is similar to that shown by the oxidation product of tetramethyldihydrobrazileinol with hydrogen peroxide (Engels, Perkin, and Robinson, *loc. cit.*).

Deoxytrimethylbrazilone Dibromide (VI).—This substance is precipitated, when its components are mixed in acetic acid solution, in glistening, dark crimson needles and it may also be obtained by the addition of a solution of bromine in light petroleum to deoxytrimethylbrazilone dissolved in chloroform. Accurate analytical figures could not be obtained on account of two properties. When kept in a desiccator, the substance loses bromine with the formation of the *iso*brazilein salt (Found: Br, 22·0. Calc.: Br, 20·7%. *Found in a specimen kept only 20 minutes: Br, 25·8%*). Secondly, with an excess of bromine a *perbromide* is precipitated (Found: Br, 61·5. $C_{19}H_{18}O_4Br_6$ requires Br, 60·9%). The substance gives carmine solutions and its other properties are mentioned in the introductory section.

Dihydrodeoxytrimethylbrazilone (IX).—This substance, which might also be conveniently named O-*trimethylbrazilane*, was obtained by shaking a solution of deoxytrimethylbrazilone (2·5 g.) in ethyl acetate (200 c.c.), containing norite (1 g.) and 1% palladous chloride (10 c.c.), with hydrogen. Absorption of the gas was rapid at first and when it slackened the temperature of the mixture was raised to 40°. The *dihydro*-derivative separated from the concentrated, filtered solution and after twice crystallising from methyl alcohol was obtained in colourless, transparent, rod-like needles, m. p. 109° (Found: C, 72·7; H, 6·5. $C_{19}H_{20}O_4$ requires C, 73·1; H, 6·4%). This substance does not exhibit such characteristic colour-reactions as does deoxytrimethylbrazilone. On warming its pale yellow solution in concentrated sulphuric acid, a deeper yellow solution exhibiting a faint green fluorescence is obtained. The brownish-red solution in cold concentrated nitric acid on dilution with water also exhibits a weak green fluorescence.

Synthesis of Trimethylbrazilone (X).—A solution of chromic acid (0·8 g.) in water (3 c.c.) was gradually added to one of dihydrodeoxytrimethylbrazilone (1·0 g.) in acetic acid (6 c.c.) with good shaking; the temperature was kept below 20°. After an hour the crystals that had separated were collected and quickly recrystallised from acetic acid (yield, 0·4 g.), forming almost colourless prisms, m. p. 185° when rapidly heated (Found: C, 66·6; H, 5·7. Calc. for $C_{19}H_{18}O_6$: C, 66·7; H, 5·2%). The melting point of a quickly heated, intimate mixture with an authentic specimen of trimethylbrazilone was also

185°. The identity was further confirmed by the formation of α-anhydrotrimethylbrazilone by the action of aqueous sodium hydroxide and of acetyl-α-anhydrotrimethylbrazilone by the action of acetic anhydride. The blue-green colour reaction with alcoholic potassium hydroxide and chloroform and the highly characteristic behaviour with concentrated nitric acid and of the product (nitrohydroxydihydrotrimethylbrazilone) with alcoholic potassium hydroxide were also observed.

Reduction of Trimethylbrazilone by Means of Amalgamated Aluminium.—Aluminium foil (1 g.) was amalgamated and added to a solution of trimethylbrazilone (2 g.) in ethyl acetate (200 c.c.) and after some time the temperature was raised to 50—60°. After 8 hours the filtered solution was concentrated in a vacuum; the residue crystallised from hot aqueous alcohol in colourless rods, m. p. 129° with evolution of gas (Found: C, 64·2; H, 6·0. $C_{19}H_{20}O_6,0{\cdot}5H_2O$ requires C, 64·6; H, 6·0%). This view of the composition of the substance is put forward provisionally. The analyses fitted the formula $C_{23}H_{26}O_8$ ($C_{19}H_{18}O_6,CH_3{\cdot}CO_2Et$) and the reduction was therefore carried out in moist benzene instead of ethyl acetate solution, with the result that the same substance was isolated.

This reduction product dissolves in sulphuric acid to a deep violet solution and on gentle warming this becomes brown and develops an intense green fluorescence. The colour of the fluorescence is, however, much duller than that due to the *iso*brazilein salts and it becomes very weak on dilution of the sulphuric acid with water. The reaction is reminiscent of the behaviour of certain substances in the α-anhydrotrimethylbrazilone series and suggests that the new compound is similarly constituted. The action of acetic anhydride on this substance leads to the formation of a crystalline *derivative*, m. p. 116°, which greatly depresses the m. p. of acetyl-α-anhydrotrimethylbrazilone. When heated at 80° for 3 hours in a vacuum, the substance lost 4·7%, but it is highly probable that this figure is not significant owing to the decomposition that accompanied dehydration.

We suggest tentatively that this substance is the secondary alcohol related to the aldol-type tautomeride of trimethylbrazilone and that the action of acetic anhydride dehydrates it to deoxy-α-anhydrotrimethylbrazilone. This matter will be further investigated.

Trimethyldihydrobrazilone (*Hydroxy-O-trimethylbrazilin, Dihydroxy-O-trimethylbrazilane, iso*Trimethyldihydrobrazileinol) (XI).—This intramolecular pinacol of trimethylbrazilone was obtained in the following manner: Acetic acid (20 c.c.) was added in small portions

to a solution of trimethylbrazilone (2·0 g.) in alcohol (300 c.c.) mixed with a large excess of zinc dust, the temperature being maintained at about 45° and the flask well shaken from time to time. After remaining over-night at room temperature, the product was isolated from the filtered solution by evaporation in a good vacuum, treatment of the residue with water and ethyl acetate and of the residue from the ethyl acetate layer with alcohol. The crystalline paste was drained and the substance recrystallised from not too much alcohol, forming stout, colourless prisms, m. p. 167—168° (Found in material dried in a vacuum desiccator: C, 65·5; H, 5·6. Found in material dried at 110° in a vacuum: C, 65·8; H, 5·8. $C_{19}H_{20}O_6$ requires C, 66·2; H, 5·8%). This *pinacol* adheres tenaciously to some water, but apparently not in any simple molecular ratio; the anhydrous material acquired a salmon-pink colour but its m. p. was unchanged. It dissolves in concentrated hydrochloric acid to a crimson-scarlet solution, and in sulphuric acid to a carmine solution that rapidly becomes brownish-yellow and acquires very intense yellowish-green fluorescence, persistent on dilution with water; unless the solution is very dilute, on addition of water to the sulphuric acid an orange, crystalline precipitate is obtained, and this was identified as *iso*brazilein trimethyl ether hydrogen sulphate by conversion into the corresponding ferrichloride and careful comparison with an authentic specimen. This behaviour with sulphuric acid recalls that of trimethylbrazilein and tetramethyldihydrobrazileinol, but in the present case the *iso*brazilein derivative is more rapidly produced. This is natural, since the reaction requires the elimination of water in the case of the pinacol and of methyl alcohol in the case of the trimethylbrazilein derivatives.

The pinacol dissolves in formic acid to a crimson-scarlet solution and a *formate* slowly crystallises from this in prisms. The most characteristic salt is, however, the *anhydro-sulphate*, which crystallises in deep red needles when sulphuric acid is added to an alcoholic solution of the pinacol. It is very sparingly soluble in alcohol. The *anhydro-hydrochloride* can be similarly isolated in crimson needles, but it is more readily soluble in alcohol than the sulphate. When the salts are decomposed by water the original substance is regenerated, but the carbinol has moderately strong basic properties and in the presence of dilute mineral acid a certain amount of the quinonoid salt is always present. Our investigation of this substance is incomplete and we have good reasons for the supposition that it will be possible to modify the diphenylcarbinol grouping and to reduce it to a diphenylmethane group. It is unlikely, however, that this will be accomplished by vigorous direct reduction in strongly acid solution. A small quantity of the pinacol was dissolved

in acetic acid and a volume of concentrated hydrochloric acid half that of the solution was added. Excess of zinc dust was then introduced, and the liquid boiled for a few minutes. The neutral product, after crystallisation from alcohol, had m. p. 173° with previous softening and was identified as deoxytrimethylbrazilone by its characteristic reactions and other properties.

O-*Triacetylbrazilone* (X with OAc in place of OMe).—This account of the substance is of a preliminary character. *O*-Triacetylbrazilin (10 g.), dissolved in acetic acid (40 c.c.), was oxidised at 15° by chromic acid (6 g. in 8 c.c. of water) which was gradually introduced. The prismatic needles that were deposited were isolated after 4 hours and crystallised from alcohol; m. p. 187° (decomp.) (Found: C, 61·1; H, 4·4. $C_{22}H_{18}O_9,0{\cdot}5H_2O$ requires C, 60·7; H, 4·4%. Found in material dried at 110° in a vacuum: C, 61·9; H, 4·2. $C_{22}H_{18}O_9$ requires C, 62·0; H, 4·2%). The solution in sulphuric acid is deep orange-yellow. When a little potassium hydroxide is added to an alcoholic solution of the substance a yellow coloration, changing to green and then brown, is produced.

O-*Tribenzoylbrazilone* was similarly obtained by the oxidation of *O*-tribenzoylbrazilin with chromic acid; it crystallised from alcohol in colourless prisms, m. p. 205° (decomp.) (Found: C, 72·6; H, 4·0. $C_{37}H_{24}O_9$ requires C, 72·5; H, 3·9%).

This investigation is being continued.

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CXCIX.—*The Action of Certain Dibromotetracarboxylic Esters on the Sodium Derivatives of Ethyl Malonate, Ethyl Ethanetetracarboxylate, and Analogous Substances.*

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WHEN a dibromo-hydrocarbon reacts with the sodium derivative of ethyl malonate, the decomposition usually proceeds in such a manner that sodium bromide is eliminated and a *cyclo*paraffin dicarboxylic ester is produced; in the case of trimethylene dibromide, for example, the following change occurs:

$$CH_2Br{\cdot}CH_2{\cdot}CH_2Br \xrightarrow{2CHNa(CO_2Et)_2} CH_2{<}{CH_2 \atop CH_2}{>}C(CO_2Et)_2 + CH_2(CO_2Et)_2$$

A similar decomposition takes place when the dibromo-hydrocarbon is replaced by the corresponding dibromodicarboxylic ester

containing CO_2Et associated with each bromine atom; *e.g.*, $\alpha\gamma$-dibromopropane-$\alpha\gamma$-dicarboxylic ester reacts with ethyl sodiomalonate to yield ethyl *cyclo*butane-1 : 2 : 2 : 3-tetracarboxylate :

$$\begin{array}{l} CH_2\cdot CHBr\cdot CO_2Et \\ CHBr\cdot CO_2Et \end{array} \longrightarrow \begin{array}{l} CH_2 \text{———} CH\cdot CO_2Et \\ CH(CO_2Et)\cdot C(CO_2Et)_2 \end{array}$$

(Ing and Perkin, J., 1925, **127**, 2389). But if an $\alpha\gamma$-dibromo-$\alpha\alpha\gamma\gamma$-tetracarboxylic ester such as $(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2$ is employed in the place of the $\alpha\gamma$-dibromo-$\alpha\gamma$-dicarboxylic ester, interaction of an entirely different type occurs. The first case of this kind was observed by Perkin and Prentice (J., 1891, **59**, 822), who, in studying the interaction of ethyl $\alpha\epsilon$-dibromopentane-$\alpha\alpha\epsilon\epsilon$-tetracarboxylate with the sodium derivative of ethyl malonate, found that instead of ethyl *cyclo*hexane-1 : 1 : 2 : 2 : 3 : 3-hexacarboxylate being formed as analogy had suggested, the product consisted of a mixture of ethyl *cyclo*pentane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethanetetracarboxylate, the change having evidently taken the following course :

$$(CO_2Et)_2CBr\cdot[CH_2]_3\cdot CBr(CO_2Et)_2 + 2CHNa(CO_2Et)_2 \longrightarrow$$

$$\begin{array}{c} CH_2\cdot CH_2\cdot CH_2 \\ (CO_2Et)_2C \text{———} C(CO_2Et)_2 \end{array} + (CO_2Et)_2CH\cdot CH(CO_2Et)_2.$$

It was suggested at the time that the curious course taken by this interaction was due to the greater ease of formation of the *cyclo*pentane ring. At a later date (J., 1903, **83**, 782; 1905, **87**, 358) Gregory and Perkin showed that the interaction of ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate with the disodium derivative of ethyl propane-$\alpha\alpha\gamma\gamma$-tetracarhoxylate does not lead to the synthesis of the *cyclo*hexane derivative as had been expected but to the formation of two molecules of ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate, the yield being almost quantitative :

$$(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2 + (CO_2Et)_2CNa\cdot CH_2\cdot CNa(CO_2Et)_2$$

$$\longrightarrow 2CH_2 < \begin{array}{l} C(CO_2Et)_2 \\ C(CO_2Et)_2 \end{array}$$

The present investigation was undertaken with the object of studying other decompositions of the kind just mentioned, under as varied conditions as practicable, and it was hoped that it might then be possible to suggest some satisfactory explanation to account for the curious course these interactions take. The following brief summary will indicate sufficiently well the cases which were selected for examination and the course followed by each of the decompositions.

I. Ethyl dibromomalonate and ethyl disodioethanetetracarb-

oxylate interact with the formation of ethyl ethylenetetracarboxylate :

$$2CBr_2(CO_2Et)_2 + 2(CO_2Et)_2CNa{\cdot}CNa(CO_2Et)_2 \longrightarrow 3(CO_2Et)_2C{:}C(CO_2Et)_2$$

II. Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate and ethyl sodiomalonate yield ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethanetetracarboxylate :

$$(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CBr(CO_2Et)_2 + 2CHNa(CO_2Et)_2 \longrightarrow CH_2{<}\begin{matrix}C(CO_2Et)_2\\ |\\ C(CO_2Et)_2\end{matrix} + (CO_2Et)_2CH{\cdot}CH(CO_2Et)_2$$

III. Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate interacts with ethyl disodioethanetetracarboxylate to yield ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethylenetetracarboxylate :

$$(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CBr(CO_2Et)_2 + (CO_2Et)_2CNa{\cdot}CNa(CO_2Et)_2 \longrightarrow CH_2{<}\begin{matrix}C(CO_2Et)_2\\ |\\ C(CO_2Et)_2\end{matrix} + (CO_2Et)_2C{:}C(CO_2Et)_2$$

IV. Ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate and ethyl sodiomalonate yield ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethanetetracarboxylate :

$$(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CBr(CO_2Et)_2 + 2CHNa(CO_2Et)_2 \longrightarrow \begin{matrix}CH_2-C(CO_2Et)_2\\ |\qquad\ |\\ CH_2-C(CO_2Et)_2\end{matrix} + (CO_2Et)_2CH{\cdot}CH(CO_2Et)_2$$

V. Ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate reacts with ethyl disodioethanetetracarboxylate to yield ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethylenetetracarboxylate :

$$(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CBr(CO_2Et)_2 + (CO_2Et)_2CNa{\cdot}CNa(CO_2Et)_2 \longrightarrow \begin{matrix}CH_2-C(CO_2Et)_2\\ |\qquad\ |\\ CH_2-C(CO_2Et)_2\end{matrix} + (CO_2Et)_2C{:}C(CO_2Et)_2$$

VI. Ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate and ethyl disodiobutane-$\alpha\alpha\delta\delta$-tetracarboxylate interact with the formation of two molecules of ethyl *cyclo*butane-1 : 1 : 2 : 2-tetracarboxylate :

$$(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CBr(CO_2Et)_2 + (CO_2Et)_2CNa{\cdot}CH_2{\cdot}CH_2{\cdot}CNa(CO_2Et)_2 \longrightarrow 2\begin{matrix}CH_2-C(CO_2Et)_2\\ |\qquad\ |\\ CH_2-C(CO_2Et)_2\end{matrix}$$

Various explanations for the apparently anomalous course of these decompositions have been considered from time to time. It has been suggested that in case III, for example, there may in the

first place be an interchange of bromine and sodium giving rise to the molecules $(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CNa(CO_2Et)_2$ and

$$(CO_2Et)_2CBr{\cdot}CNa(CO_2Et)_2$$

and that each of these might undergo internal elimination of sodium bromide with the formation of ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate and ethyl ethylenetetracarboxylate respectively. In a similar way, in case VI, ethyl dibromobutanetetracarboxylate and the disodium derivative of ethyl butanetetracarboxylate might undergo intermolecular change yielding two molecules of $(CO_2Et)_2CBr{\cdot}CH_2{\cdot}CH_2{\cdot}CNa(CO_2Et)_2$, each of which might then suffer internal elimination of sodium bromide with the formation of ethyl *cyclo*butanetetracarboxylate. Interpreted in accordance with modern conceptions, this suggestion is probably fundamentally correct, but, in this form, it does not appear to be capable of development into an explanation of the whole of the phenomena.

Another view is that the reason for the course taken in these interactions is to be sought in an extension of the theory of Beasley, Ingold, and Thorpe (J., 1915, **107**, 1080). If in the case of ethyl propane-$\alpha\alpha\gamma\gamma$-tetracarboxylate, for example, it is assumed that the two pairs of carbethoxy-groups cause the fourth valencies of the two carbon atoms to which they are united to be directed together, then it is conceivable that the valencies set free in each of the molecules when sodium bromide is eliminated might, by nature of their proximity, unite directly rather than combine with the second molecule, and that, even in case IV, this might be sufficient to cause the *cyclo*butane derivative to be produced rather than the *cyclo*pentane derivative. Ingold (J., 1921, **119**, 305) has calculated that the carboxyl group attached to a carbon atom decreases the angle between two of the remaining valencies by the same amount as the methyl group, namely, by 2° 8′. It is of course possible that two carbethoxy-groups attached to the same carbon atom might cause a deflexion of more than 5° 6′, but in any case the influence would be too inconsiderable to account for the formation of the small rings in the examples given in this communication.

A much more likely explanation, and one which quite easily meets all the cases under discussion, is the following, for which we are indebted to Professor Robinson.

It seems probable on general grounds that in cases where competing intramolecular and intermolecular reactions of a similar type may occur, there will be a factor favouring the former processes. The inevitable proximity of the reacting centres involves a virtual relative increase of concentration or active mass and obviously there is a stage that is unimolecular in the intramolecular processes, but bimolecular in the intermolecular processes. Thus the action

of metals on trimethylene bromide might give either *cyclo*propane or *cyclo*hexane and on the basis of the principle of maximal loss of free energy we should anticipate the formation of *cyclo*hexane. Actually it is *cyclo*propane that is formed and the consideration mentioned above suggests a reasonable explanation of the result. It is not practicable in this instance to augment the concentration of the bromide to such a degree that the intermolecular reaction occurs to a predominating extent, but in cases where the intramolecular reaction proceeds with greater difficulty it should be possible to observe the effects of variations of the concentration on the proportions in which the products are obtained.

We may therefore conclude that substances of the types

$$(CO_2Et)_2CBr\cdot\bar{C}(CO_2Et)_2\}\overset{+}{N}a, \quad (CO_2Et)_2CBr\cdot[CH_2]_n\cdot\bar{C}(CO_2Et)_2\}\overset{+}{N}a$$

would be far more likely to give $(CO_2Et)_2C{:}C(CO_2Et)_2$ and $(CO_2Et)_2C\cdot[CH_2]_n\cdot C(CO_2Et)_2$ (ring closed between the two C atoms) than to give products arising from intermolecular reactions, provided that n is not too great. The intramolecular processes are of a particularly facile character and involve merely the transfer of a negative charge to the bromine atom, a species of oxidation–reduction mechanism being postulated. It is necessary, however, if the results described in this communication are to be accommodated, to recognise in addition that the contrast between the behaviour of ethyl $\alpha\gamma$-dibromoglutarate and its $\alpha\gamma$-dicarbethoxy-derivative (see p. 1514) is due to the fact that it is only the α-bromomalonic esters (among substances here considered) that contain a bromine atom analogous to that of the hypobromites and capable of substituting itself for hydrogen in suitably reactive molecules. So avid of electrons is the bromine of the bromomalonic esters of the type $CRBr(CO_2Et)_2$ that the substances behave as oxidising agents, liberating iodine from potassium iodide (compare the behaviour of ethyl α-bromoaceto-acetate in Kurt Meyer's method of titration of enols with bromine) and oxidising hydrazine to nitrogen (Hirst and Macbeth, J., 1922, **121**, 904, 1116; compare *Ann. Reports*, 1922, **19**, 98—103). Orton and King (J., 1911, **99**, 1185) and Wohl (*Ber.*, 1919, **52**, 51) have suggested the use of halogenated amides in halogenations and Gupta and Thorpe (J., 1922, **121**, 1896) showed that dibromodimethyl-dihydroresorcinol reacts quantitatively with dimethylaniline with formation of *p*-bromodimethylaniline. Halogenation with the help of bromomalonic esters has, however, not been observed previously and is described in the sequel. All the reactions discussed in this communication can be correlated by the assumption of rapid bromination of substituted sodiomalonic esters by substituted bromomalonic esters, followed by slower double decom-

positions of the normal type concerned with alkylation of malonic esters. A few examples are symbolised below and other cases appear to conform to these types. (*Alternative views may be taken of the course of the interaction of bromine and ethyl sodiomalonate. Two anions from the ester may transfer their charges directly to a bromine molecule or the first phase may be bimolecular, leading to the formation of ethyl bromomalonate and sodium bromide.* Schemes analogous to the latter view have been adopted in the text, but the translation into the corresponding schemes employing the direct transfer of charges and formation of bromidions can be made without difficulty. Both courses are possible and may occur simultaneously.)

A. 1. $(CO_2Et)_2CBr\cdot[CH_2]_3\cdot CBr(CO_2Et)_2 + \bar{C}H(CO_2Et)_2\}\overset{+}{Na} \longrightarrow$
$(CO_2Et)_2CBr\cdot[CH_2]_3\cdot\bar{C}(CO_2Et)_2\}\overset{+}{Na} + CHBr(CO_2Et)_2$
$\downarrow$

2. $(CO_2Et)_2C\cdot[CH_2]_3\cdot C(CO_2Et)_2 + Na\}Br.$ (ring closed between the two C atoms)

3. $\bar{C}H(CO_2Et)_2\}\overset{+}{Na} + CHBr(CO_2Et)_2 \longrightarrow$
$(CO_2Et)_2CH\cdot CH(CO_2Et)_2 + Na\}Br$

B. 1. $(CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2 +$
$(CO_2Et)_2CH\cdot CH_2\cdot\bar{C}(CO_2Et)_2\}\overset{+}{Na} + Na\}OEt$
$\longrightarrow (CO_2Et)_2CBr\cdot CH_2\cdot\bar{C}(CO_2Et)_2\}\overset{+}{Na} +$
$\downarrow \qquad \overset{+}{Na}\{(CO_2Et)_2\bar{C}\cdot CH_2\cdot CBr(CO_2Et)_2 + EtOH$

2. $(CO_2Et)_2C\cdot CH_2\cdot C(CO_2Et)_2 + Na\}Br$ (ring closed between the two C atoms)

C. 1. $2CBr_2(CO_2Et)_2 + 2(CO_2Et)_2CH\cdot\bar{C}(CO_2Et)_2\}\overset{+}{Na} \longrightarrow$
$2(CO_2Et)_2\bar{C}\cdot CBr(CO_2Et)_2\}\overset{+}{Na} + 2CHBr(CO_2Et)_2$

2. $(CO_2Et)_2\bar{C}\cdot CBr(CO_2Et)_2\}\overset{+}{Na} \longrightarrow (CO_2Et)_2C{:}C(CO_2Et)_2 + Na\}Br$

3. $2CHBr(CO_2Et)_2 + Na\}OEt \longrightarrow (CO_2Et)_2CH\cdot CBr(CO_2Et)_2 +$
$Na\}Br + EtOH$

4. $(CO_2Et)_2CH\cdot CBr(CO_2Et)_2 + Na\}OEt \longrightarrow$
$(CO_2Et)_2C{:}C(CO_2Et)_2 + Na\}Br + EtOH$

In order to bring further evidence of the oxidising action of bromo-esters containing the α-bromo-αα-dicarboxylic group, the action of ethyl αγ-dibromopropane-ααγγ-tetracarboxylate and of ethyl αδ-dibromobutane-ααδδ-tetracarboxylate on phenol was investigated.

When the former was heated to boiling with a large excess of phenol, the phenol was brominated and the product, on hydrolysis, yielded *propane-ααγ-tricarboxylic acid*, $CO_2H·CH_2·CH_2·CH(CO_2H)_2$, m. p. 125°, which on heating, decomposed into carbon dioxide and glutaric acid (m. p. 97—98°). Clearly the products of this decomposition are brominated phenol and ethyl propane-ααγγ-tetracarboxylate, bromination of the phenol and reduction of the dibromo-ester having taken place. In a similar manner, ethyl αδ-dibromobutane-ααδδ-tetracarboxylate and phenol interacted smoothly to yield brominated phenol and an ester which was clearly ethyl butane-ααδδ-tetracarboxylate because on hydrolysis by boiling with hydrochloric acid an almost quantitative yield of adipic acid was obtained.

It is therefore each $CBr(CO_2Et)_2$ grouping which is equivalent to a molecule of bromine in these reactions. If, for example, ethyl αδ-dibromobutane-ααδδ-tetracarboxylate could be regarded as equivalent to a molecule of the *cyclo*butane ester plus a molecule of bromine, the experiment just described should have yielded the ring-ester and hydrogen bromide. That this was not the case supports the view that the ring formation, observed in the reactions previously discussed, is dependent on the intermediate production of the sodio-derivative of ethyl monobromobutane-tetracarboxylate. In order to test this hypothesis still further, the following experiment was instituted:

Ethyl αγ-dibromopropane-ααγγ-tetracarboxylate (1 mol.) was heated in alcoholic solution with β-naphthol (1 mol.) and sodium ethoxide (2 mols.) on the steam-bath. The product, after being boiled with dilute hydrochloric acid and concentrated, gave a large yield of *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylic acid, the interaction having evidently taken place on these lines:

$$C_{10}H_7·ONa + NaOEt + (CO_2Et)_2CBr·CH_2·CBr(CO_2Et)_2 \longrightarrow$$
$$C_{10}H_6Br·ONa + (CO_2Et)_2CH·CH_2·CBr(CO_2Et)_2 \longrightarrow$$
$$C_{10}H_6Br·OH + (CO_2Et)_2CNa·CH_2·CBr(CO_2Et)_2 \longrightarrow$$
$$CH_2<\begin{matrix}C(CO_2Et)_2\\|\\C(CO_2Et)_2\end{matrix}.$$

This experiment emphasises the necessity for the formation of the sodio-bromo-derivative before the ring can be closed.

Included in this investigation are some further experiments on the abnormal behaviour of the disodium derivative of ethyl pentane-hexacarboxylate, one of the substances produced in considerable quantity during the condensation of ethyl malonate with formaldehyde (Bottomley and Perkin, J., 1900, 77, 298). In the course of that investigation it was shown that the disodium derivative of this

ester does not react normally when heated with methylene iodide to yield ethyl *cyclo*hexane-1 : 1 : 3 : 3 : 5 : 5-hexacarboxylate but is almost completely decomposed into ethyl paramethylenemalonate, probably thus,

$$(CO_2Et)_2CNa{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CNa(CO_2Et)_2 \longrightarrow 2CH_2{:}C(CO_2Et)_2 + Na_2C(CO_2Et)_2$$

the disodium derivative of ethyl malonate then reacting with the methylene iodide to yield a further quantity of ethyl paramethylenemalonate. That the disodium derivative of ethyl pentanehexacarboxylate is in fact capable of existence was demonstrated by its conversion into ethyl *cyclo*pentane-1 : 1 : 3 : 3 : 4 : 4-hexacarboxylate by the action of bromine (*loc. cit.*, p. 303).

$$(CO_2Et)_2C{<}\begin{matrix}CH_2{\cdot}CNa(CO_2Et)_2\\CH_2{\cdot}CNa(CO_2Et)_2\end{matrix} + Br_2 \longrightarrow (CO_2Et)_2C{<}\begin{matrix}CH_2{\cdot}\underset{|}{C}(CO_2Et)_2\\CH_2{\cdot}C(CO_2Et)_2\end{matrix}$$

A characteristic of this ester is that, on hydrolysis and elimination of carbon dioxide, it yields *trans-cyclo*pentane-1 : 2 : 4-tricarboxylic acid, m. p. 129—130°.

We have now found that the disodium derivative of ethyl *pentanehexacarboxylate on heating with ethyl αβ-dibromopropionate*, instead of reacting normally with the formation of the *cyclo*heptane derivative, yields ethyl *cyclo*pentanepentacarboxylate. The product was again identified by conversion into *trans-cyclo*pentanetricarboxylic acid, m. p. 129—130°. The probable explanation of this curious synthesis is that the disodium derivative of ethyl pentanehexacarboxylate is, on heating, first decomposed into ethyl paramethylenemalonate and the disodium derivative of ethyl propane-ααγγ-tetracarboxylate, which then reacts with the ethyl αβ-dibromopropionate to yield ethyl *cyclo*pentane-1 : 2 : 2 : 4 : 4-pentacarboxylate :

$$(CO_2Et)_2CNa{\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CNa(CO_2Et)_2 \longrightarrow CH_2{:}C(CO_2Et)_2 + (CO_2Et)_2CNa{\cdot}CH_2{\cdot}CNa(CO_2Et)_2 \xrightarrow{CH_2Br{\cdot}CHBr{\cdot}CO_2Et} (CO_2Et)_2C{<}\begin{matrix}CH_2{\cdot}\underset{|}{C}(CO_2Et)_2\\CH_2{\cdot}CH{\cdot}CO_2Et\end{matrix}.$$

Goldsworthy and Perkin (J., 1914, **105**, 2671) have already shown that an excellent yield of ethyl *cyclo*pentanepentacarboxylate may be obtained by treating the disodium derivative of ethyl propanetetracarboxylate with ethyl dibromopropionate. The ease with which ethyl pentanehexacarboxylate loses a molecule of ethyl paramethylenemalonate when its disodium derivative is heated still requires explanation.

EXPERIMENTAL.

Preparation of the Materials employed in the Following Experiments.—"Absolute alcohol" was dehydrated as completely as possible by boiling under reflux over quicklime for at least 8 hours and then distilled.

Ethyl ethanetetracarboxylate, $(CO_2Et)_2CH·CH(CO_2Et)_2$, was prepared by the action of an ethereal solution of iodine on the sodium derivative of ethyl malonate under the conditions described by Bischoff and Rach (*Ber.*, 1884, **17**, 2781). Ethyl propane-$\alpha\alpha\gamma\gamma$-tetracarboxylate, $(CO_2Et)_2CH·CH_2·CH(CO_2Et)_2$, was obtained by the action of formaldehyde on ethyl malonate in the presence of diethylamine (Knoevenagel, *Ber.*, 1894, **27**, 2346; Haworth and Perkin, J., 1897, **71**, 1063) and distilled at 195—197°/14 mm. Ethyl butane-$\alpha\alpha\delta\delta$-tetracarboxylate, $(CO_2Et)_2CH·CH_2·CH_2·CH(CO_2Et)_2$, was prepared by the action of ethyl sodiomalonate on ethylene chloride and on ethyl *cyclo*propane-1 : 1-dicarboxylate (Perkin, J., 1894, **65**, 578; Bone and Perkin, J., 1895, **67**, 111; compare Lean and Lees, J., 1897, **71**, 1063). It distilled at 211—215°/14 mm.

Ethyl $\alpha\gamma$-dibromopropane-$\alpha\alpha\gamma\gamma$-tetracarboxylate,

$$(CO_2Et)_2CBr·CH_2·CBr(CO_2Et)_2,$$

was obtained by the action of bromine on ethyl propane-$\alpha\alpha\gamma\gamma$-tetracarboxylate in chloroform solution (Gregory and Perkin, J., 1903, **83**, 782). This substance is best purified by cooling a saturated solution in warm petroleum (b. p. 60—80°) to −20° and melts at 55°. Ethyl $\alpha\delta$-dibromobutane-$\alpha\alpha\delta\delta$-tetracarboxylate, $(CO_2Et)_2CBr·CH_2·CH_2·CBr(CO_2Et)_2$, m. p. 83—85°, was prepared by the action of bromine on ethyl butanetetracarboxylate under conditions similar to those used in the preparation of the corresponding dibromopropane ester (compare Lean, J., 1900, **77**, 107). Ethyl dibromomalonate was obtained by the action of bromine on ethyl malonate as described by Conrad and Bruckner (*Ber.*, 1891, **24**, 3001) and was collected at 128—132°/15 mm.

The decompositions briefly outlined in the introduction were carried out under the following conditions:

I. Ethyl dibromomalonate (31·8 g.) was added to an alcoholic solution of the disodium derivative from ethyl ethanetetracarboxylate (31·8 g.); the mixture became warm and sodium bromide separated. After the whole had been heated under reflux on the steam-bath for 2 hours, water was added, and the product isolated by extraction with ether as usual. A colourless syrup was obtained which largely solidified when it was cooled to −15° and well stirred. The solid was collected with the aid of a pump, left in contact with porous porcelain, and recrystallised from petroleum; it then melted at 56° and was found to be ethyl ethylenetetracarboxylate. The

oil which passed through the filter yielded on distillation a further quantity of ethyl ethylenetetracarboxylate, the yield of this ester being about 60% of that possible. The final mother-liquor contained the same ester and yielded on hydrolysis and elimination of carbon dioxide, besides fumaric acid, about 3 g. of succinic acid derived evidently from some unchanged ethyl ethanetetracarboxylate.

II. When ethyl αγ-dibromopropane-ααγγ-tetracarboxylate (1 mol.) was added to an alcoholic solution of ethyl sodiomalonate (2 mols.), the mixture became warm and sodium bromide separated. The reaction was complete after 2 hours' refluxing and the product, isolated by addition of water and extraction with ether, was a viscid oil which gradually deposited crystals; after recrystallisation from light petroleum, the substance melted at 75—76° and consisted of ethyl ethanetetracarboxylate. The oily mother-liquor solidified on being cooled to −15° and, after contact with porous porcelain, and several crystallisations from petroleum, a substance, m. p. 40—41°, was obtained which was shown to be ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate by analysis and by the undepressed melting point of its mixture with an equal amount of this substance prepared as explained on p. 1514.

III. Ethyl αγ-dibromopropane-ααγγ-tetracarboxylate (24·5 g.) was added to ethyl ethanetetracarboxylate (15·9 g.) dissolved in an alcoholic solution of sodium ethoxide (2·3 g. Na). The interaction which set in on standing, was complete after 1 hour's heating under reflux on the steam-bath. The product, diluted with water, was extracted with ether and the ethereal solution was washed with sodium carbonate, dried over calcium chloride, and evaporated; a solid was then obtained which was separated into its two components by fractional crystallisation from petroleum. The less soluble substance, m. p. 55—57°, was ethyl ethylenetetracarboxylate and the other substance, m. p. 42—44°, was proved by careful comparison to be ethyl *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylate.

IV. On adding ethyl αδ-dibromobutane-ααδδ-tetracarboxylate (25·2 g.) to a solution of ethyl malonate (16 g.) in alcoholic sodium ethoxide (2·5 g. Na), sodium bromide was quickly precipitated; the decomposition was complete after 2 hours' heating under reflux. The product, isolated in the usual way, was a pale brown syrup which, on cooling, partly solidified. The solid, collected by means of the pump and crystallised from petroleum, melted at 75—76° and proved to be ethyl ethanetetracarboxylate. The oily mother-liquor was hydrolysed by boiling with dilute hydrochloric acid for several hours, and the solution concentrated first on the steam-bath and then over caustic potash in a vacuum desiccator. The solid

which had separated after some days was collected and crystallised from hydrochloric acid; a small quantity of adipic acid was isolated and the mother-liquor contained some succinic acid. The former resulted evidently from the hydrolysis of some ethyl butanetetracarboxylate which had been produced by the reduction of the dibromo-derivative, and the latter from some unchanged ethanetetracarboxylate which had not crystallised. The hydrochloric acid mother-liquor from these acids yielded, on evaporation to dryness, a syrupy acid which was converted, by boiling with excess of acetyl chloride, into an anhydride which distilled at 165—170°/20 mm., solidified, and melted at 71—73°. This was identified as the anhydride of *cis-cyclo*butane-1 : 2-dicarboxylic acid by conversion into the acid, m. p. 136—138°, by boiling with water (Perkin, J., 1894, **65**, 582).

V. On mixing equimolecular proportions of ethyl αδ-dibromobutane-ααδδ-tetracarboxylate and ethyl disodioethanetetracarboxylate in alcoholic solution, interaction set in at once; it was completed by heating under reflux for ½ hour. The product, isolated in the usual manner, was a viscid oil which at −10° gradually deposited a solid; this, after recrystallisation, melted at 55—57° and proved to be ethyl ethylenetetracarboxylate. The oily mother-liquor was hydrolysed by boiling with dilute hydrochloric acid for some hours and concentrated; a little fumaric acid then separated and was identified by conversion into maleic anhydride. The mother-liquor was evaporated to dryness and the syrupy residue was heated in an oil-bath at 180° until evolution of carbon dioxide had ceased and then digested with excess of acetyl chloride for 2 hours. On distillation, an anhydride was obtained which boiled at 165°/20 mm. and solidified to a crystalline mass, m. p. 62—70°. This was decomposed by boiling with water, and the solution allowed to evaporate over sulphuric acid in a vacuum desiccator; a solid was then obtained from which, by crystallisation from hydrochloric acid, *cis-cyclo*butane-1 : 2-dicarboxylic acid, m. p. 136—137°, was isolated in quantity.

VI. On the addition of ethyl dibromobutanetetracarboxylate (25·2 g.) to a solution of ethyl butanetetracarboxylate (17·3 g.) in alcoholic sodium ethoxide (2·3 g. Na), the mixture became warm and sodium bromide separated. The action was completed by heating under reflux for 1 hour and the product was treated with water and extracted with ether. The syrup remaining after evaporation of the ether was hydrolysed by boiling with dilute hydrochloric acid for several hours, the solution was evaporated, and the syrupy residue heated at 180° until evolution of gas had ceased and then refluxed for 2 hours with acetyl chloride. On distillation, an oil,

b. p. 148°/14 mm., was obtained which quickly solidified and after contact with porous porcelain had m. p. 72—74°. When this anhydride was boiled with water, and the solution allowed to concentrate over sulphuric acid in a vacuum desiccator, *cis-cyclo*butane-1 : 2-dicarboxylic acid was obtained, m. p. 137—138° (Found: C, 49·9; H, 5·7. Calc. for $C_6H_8O_4$: C, 50·0; H, 5·6%).

The Action of Phenol on (i) *Ethyl αγ-Dibromopropane-ααγγ-tetracarboxylate and* (ii) *Ethyl αδ-Dibromobutane-ααδδ-tetracarboxylate.*—(i) Ethyl αγ-dibromopropane-ααγγ-tetracarboxylate (22 g.), mixed with phenol (70 g.), was gently boiled under reflux for 5 hours and the product, which, on cooling partly crystallised, was distilled; a mixture of phenol and brominated phenol passed over at 185—190° and crystallised, a thermometer placed in the solidifying mass remaining at 35°. The residue above 190° was boiled for 6 hours with concentrated hydrochloric acid (30 c.c.) and water (40 c.c.) and then distilled in steam to remove phenol, etc., and the solution, after being filtered from a viscid insoluble substance, was evaporated to a small bulk and left over solid potash in a vacuum desiccator for 2 weeks, during which the syrup deposited nearly pure *propane-ααγ-tricarboxylic acid*, $CO_2H \cdot CH_2 \cdot CH_2 \cdot CH(CO_2H)_2$, in balls of needles which, after contact with porous porcelain, melted at 115—118°. This acid is almost completely miscible with water, but a concentrated solution left over sulphuric acid gradually deposits needles which melt at about 125° and lose carbon dioxide at 128—135° (Found: C, 41·0; H, 4·6. $C_6H_8O_6$ requires C, 40·9; H, 4·5%). The acid was heated in a test-tube in a sulphuric acid bath at 150—160° until effervescence had ceased; the residue solidified, melted at 95—97° and, after crystallisation from a few drops of water, at 97—98° and consisted of glutaric acid (method of mixed melting point).

(ii) A mixture of ethyl αδ-dibromobutane-ααδδ-tetracarboxylate (20 g.) and phenol (60 g.) was heated to boiling for 6 hours and the portion boiling at 184—190°, containing much bromine, was distilled off. The residue was boiled with hydrochloric acid (30 c.c.) and water (40 c.c.) for 3 hours, the alcohol eliminated being allowed to escape; the solution was then filtered from the dark gum and evaporated to dryness. The solid residue separated from hydrochloric acid in flat needles, m. p. 150—152°, and consisted of adipic acid, the yield being almost quantitative (Found: C, 49·2; H, 6·9. Calc. for $C_6H_{10}O_4$: C, 49·3; H, 6·9%).

The Action of Ethyl αγ-Dibromopropane-ααγγ-tetracarboxylate on β-Naphthol in the Presence of Sodium Ethoxide.—The dibromo-ester (21 g.) was added to a solution of β-naphthol (6 g.) in alcoholic sodium ethoxide (Na, 2 g.), the clear liquid soon becoming cloudy. After

heating for an hour on the steam-bath, the alcohol was evaporated, and the residue was boiled with concentrated hydrochloric acid (20 c.c.) and water (50 c.c.) for 2 days, the alcohol produced being allowed to escape. The filtered product was evaporated to dryness, leaving a syrup which largely crystallised, and this was extracted with ether. After filtration, and distillation of the ether, an almost solid mass remained which, in contact with porous porcelain, left a colourless crystalline mass of nearly pure *cyclo*propane-1 : 1 : 2 : 2-tetracarboxylic acid, m. p. 205—210° and after crystallisation from a little water, 210—212° (vig. eff.) (Found: C, 38·7; H, 2·9. Calc. for $C_7H_6O_8$: C, 38·5; H, 2·7%). The identity of this acid, obtained in large yield in this process, was demonstrated by conversion into the *cis*- and *trans*-modifications of *cyclo*propane-1 : 2-dicarboxylic acid.

The Action of Ethyl αβ-Dibromopropionate on Ethyl αε-Disodiopentane-ααγγεε-hexacarboxylate.—The ethyl pentanehexacarboxylate used in this experiment was obtained from the high-boiling oil produced during the preparation of ethyl propane-ααγγ-tetracarboxylate by the condensation of ethyl malonate with formaldehyde (Bottomley and Perkin, J., 1900, 77, 298). Ethyl αβ-dibromopropionate was prepared by the addition of bromine to acraldehyde, oxidation of the product to αβ-dibromopropionic acid, and esterification of this with alcoholic hydrochloric acid. The material used distilled at 95—97°/13 mm.

A concentrated alcoholic solution of the pentane ester (25 g.) was added to a solution (50 c.c.) of sodium ethoxide (2·5 g. Na) previously mixed with an equal volume of dry ether. Ethyl dibromopropionate (13 g.) was then added, the mixture kept cool during 24 hours, the bulk of the solvents distilled off, and the residue mixed with water and extracted with ether. After being well washed, and dried over calcium chloride, the extract left on evaporation an oil, which was separated into two main fractions by distillation under reduced pressure. That boiling below 180°/15 mm. set to a wax-like solid on standing, and after contact with porous porcelain and crystallisation from alcohol, the crystals melted at 145—148° and were identified as ethyl paramethylenemalonate (Haworth and Perkin, J., 1898, 73, 340). The other fraction, b. p. 225—245°/15 mm., was boiled with hydrochloric acid until a clear solution resulted, the water and hydrochloric acid were then removed by distillation under reduced pressure, and the residual syrup was heated in an oil-bath at 180—200° for several minutes. When the solution of the product in concentrated hydrochloric acid was kept for several days over solid potash in a vacuum desiccator, crystals gradually separated; these, after being in contact with porous porce-

lain and recrystallised from hydrochloric acid, melted at 127—130° (Found : C, 47·2 ; H, 4·7. Calc. for $C_8H_{10}O_6$: C, 47·5 ; H, 4·9%). That this substance was *trans-cyclo*pentane-1 : 2 : 4-tricarboxylic acid was established by direct comparison with a specimen of this acid which had been prepared from the product of the action of ethyl αβ-dibromopropionate on the disodium derivative of ethyl propane-ααγγ-tetracarboxylate (Goldsworthy and Perkin, J., 1914, **105**, 2673).

One of us (J. J. L.) wishes to thank the Royal Commissioners of the Exhibition of 1851 for a scholarship which has enabled him to take part in this investigation, and he is also indebted to the Research Fund Committee of the Chemical Society for a grant which has defrayed part of the cost.

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CC.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XV. The Synthesis of Cyanidin Chloride by Means of* O-*Benzoylphloroglucinaldehyde.*

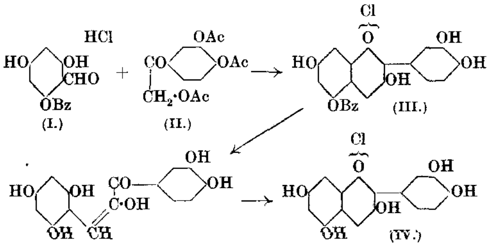
By ALEXANDER ROBERTSON and ROBERT ROBINSON.

THE methods for the syntheses of the anthocyanidins by way of their methyl ethers, unless very carefully controlled, are apt to lead to impure products in the final stage of demethylation by means of hydriodic acid in the presence of phenol. Although this difficulty can be readily overcome, it is unlikely that workers without previous experience in the group would be successful in doing so at the first attempt, and we have for some time realised the desirability of devising, if possible, a synthetic method of preparation of the pure anthocyanidins that could be used, say, as a laboratory exercise by students. The processes developed in this and the two following communications are readily carried through and result in the production of homogeneous anthocyanidins.

Direct syntheses of pelargonidin and peonidin with the aid of *O*-triacetylphloroglucinaldehyde have been already described (Nolan, Pratt, and Robinson, J., 1926, 1968), but the yields were poor and the products difficult to purify. The synthesis of cyanidin by the same method has been attempted ; it proceeds rather more smoothly but is still unsatisfactory. *O*-Benzoylphloroglucinaldehyde, on the other hand, gives good results on condensation with acetylated

derivatives of substituted ω-hydroxyacetophenones by means of hydrogen chloride, and after comparative trials we selected ethyl acetate or ethyl acetate–alcohol as the most suitable solvent. It is remarkable that in all the cases examined the acetyl groups are removed by hydrolysis from the ketonic component either in the condensation or in the crystallisation of the product, but the benzoyloxy-group remains unaffected. The products are thus the benzoylated anthocyanidins and these exhibit the alkali-colour-reactions of the corresponding anthocyanins; *e.g.*, benzoylcyanidin, benzoylpelargonidin, benzoylpeonidin, and benzoylmalvidin resemble cyanin, pelargonin, peonin, and malvin, respectively. Since the benzoyl groups are in position 5, this evidence is in agreement with the view that the disaccharide units in the anthocyanins mentioned are also in position 5.

The benzoyloxy-groups are hydrolysed by means of aqueous alcoholic sodium hydroxide, a reagent which also ruptures the pyrylium ring, and finally by treatment with hydrochloric acid the anthocyanidin is produced. The case described in the present communication is represented below.



We are deeply indebted to Geheimrath Professor R. Willstätter for kindly sending us a specimen of cyanidin chloride of natural origin. After purification of this, the identity of the natural and the synthetic material was established.

Experimental.

ω : 3 : 4-Triacetoxyacetophenone (II) was prepared by a method based on that of Voswinckel (*Ber.*, 1909, **42**, 4651). A mixture of pure ω-chloro-3 : 4-dihydroxyacetophenone (Dreczgowski, *J. Russ. Phys. Chem. Soc.*, 1893, **25**, 154) (10 g.), potassium acetate (10 g.), and acetic anhydride (40 c.c.) was heated on the steam-bath for 3 hours and then refluxed for ½ hour. The cooled product was

decomposed by water (200 c.c.). The ketone (yield, 14 g.) crystallised from carbon tetrachloride and then from methyl alcohol (charcoal) in colourless, rhombic plates, m. p. 95° (Found: C, 57·0; H, 5·0. Calc. for $C_{14}H_{14}O_7$: C, 57·1; H, 4·8%).

5-O-*Benzoylcyanidin Chloride* (III).—A solution of *O*-benzoylphloroglucinaldehyde (2·5 g.) (Part I, J., 1927, 1713) and ω:3:4-triacetoxyacetophenone (3·5 g.) in a mixture of ethyl acetate (50 c.c.) and 98% alcohol (20 c.c.) was cooled and saturated with hydrogen chloride. After 3 days the crystalline product was collected (4·6 g.); very little oxonium salt remained in the mother-liquor. When dry ethyl acetate (70 c.c.) was used instead of the mixture with alcohol, the yield was 4·0 g. of a somewhat inferior product. The crude salt (7·5 g.) was purified by solution in the minimum quantity of 80% ethyl alcohol and passage of hydrogen chloride into the solution (which boils) for 5 minutes. On cooling, the *benzoylcyanidin chloride* separated in compact crystals having a dark green appearance (5 g.). Recrystallisation was effected by solution in a mixture of boiling ethyl alcohol and 0·5% hydrochloric acid (1:1) and addition of hot 10% hydrochloric acid until there were indications of the incipient separation of solid. The cooled solution deposited dark red, slender, prismatic needles which matted together on the filter and when dried had a purplish appearance in mass. The substance was dried in a high vacuum and was then too hygroscopic to weigh accurately; it was kept in the air until the weight was constant (Found: C, 57·8; H, 4·2. $C_{22}H_{15}O_7Cl,1\cdot5H_2O$ requires C, 58·3; H, 4·0%). Benzoylcyanidin chloride dissolves in ethyl alcohol to a bluish-red solution that becomes permanganate-coloured on dilution but never violet (distinction from benzoylpelargonidin, benzoylpeonidin and benzoylmalvidin); on the addition of water a pink solution is obtained and this is rapidly decolorised on heating. The restoration of colour by the addition of hydrochloric acid is immediate but not quite complete. The solution of the salt in aqueous sodium carbonate is pure blue, and becomes a little greener on the addition of alcohol. Ferric chloride added to an alcoholic solution gives an intense deep blue coloration; on dilution with water the solution becomes reddish-violet—the reaction is identical with that exhibited by cyanidin.

Cyanidin Chloride (IV).—Benzoylcyanidin chloride (5 g.) was added to cold 8% aqueous-alcoholic sodium hydroxide (65 c.c.; solvent was 3 vols. of alcohol mixed with 2 vols. of water), air being excluded from the apparatus by nitrogen. The mixture, which was frequently agitated, was at first deep blue and gradually became dull orange-brown; after 3 hours, concentrated hydrochloric acid (100 c.c.) was added, and the whole heated at 60° until no further

increase in the intensity of the colour occurred. After being kept for 12 hours in the ice-chest, the solid was collected, washed with 5% hydrochloric acid and ether, and dried in the air (yield, 3 g.).

This product was almost pure, but was converted into the picrate, which crystallised from not too much aqueous-alcoholic picric acid in fibrous needles. The chloride regenerated in the usual manner, from a solution in methyl alcohol containing hydrogen chloride by the addition of ether, was a chocolate-brown, crystalline powder. The salt was recrystallised hy solution in alcohol, addition of 10% hydrochloric acid, and distillation of the alcohol until crystals made their appearance in the liquid. On cooling, the cyanidin chloride separated almost completely in clusters of straight, thin, chocolate-brown needles (Found: C, 52·8; H, 3·9; Cl, 10·1. Calc. for $C_{15}H_{11}O_6Cl,H_2O$: C, 52·9; H, 3·8; Cl, 10·4%).

Under other conditions the salt usually crystallises in prismatic needles or elongated rhombic prisms. The specimen exhibited all the properties of cyanidin chloride; for example, the sparing solubility in dilute sulphuric acid, the colours of acid, neutral, and alkaline alcoholic and aqueous solutions, the mode of pseudo-base formation, the precipitation of the colour-base by the addition of water to an alcoholic solution, and the ferric chloride colour reaction were all found to be normal.

The crude natural cyanidin chloride supplied by Professor Willstätter was purified through the picrate and crystallised in the manner described above for the synthetic material. A careful comparison disclosed no differences existing between the two specimens. The appearance and habit of crystallisation were identical and the solubility in 0·1% hydrochloric acid was also the same (colorimetric determination). A filtered saturated solution of the synthetic material in 0·1% hydrochloric acid dissolved no trace of the natural, and *vice versa* ; the solutions were only weakly coloured.

The natural specimen (5·08 mg.) and the synthetic (5·07 mg.) were separately dissolved in 50 c.c. of ethyl alcohol. The following description applies to both solutions, no shade of divergence being noted at any stage. The solution was dark red, bluish-red in thin layers (10 c.c. treated with 1 c.c. of dilute aqueous ferric chloride became deep blue and then rapidly changed to green and greenish-yellow; on long standing, yellowish-brown), and 40 c.c. made up to 100 c.c. with alcohol had a more bluish-red colour (colorimetric comparison). 50 C.c. of this solution were mixed with 10 c.c. of aqueous copper acetate, giving a bright blue solution which soon became greenish-blue, bluish-green, and green, successively, and the colour faded; after 12 hours, the green solutions became turbid, but if at once

heated there was a colourless precipitate and a brown film formed on the sides of the vessel. The remainder of the cyanidin solution was diluted to 100 c.c. with alcohol, giving a very bluish-red solution (colorimetric comparison) (50 c.c. treated with potassium acetate gave a violet solution and then, on the addition of hydrochloric acid, a red solution). Dilution of the remainder of the cyanidin solution to 250 c.c. with water gave a reddish-violet solution (colorimetric comparison), which became pink on acidification (colorimetric comparison); when a portion (not acidified) was heated, it became colourless, and on strong acidification with hydrochloric acid *scarcely any colour-salt was regenerated. On boiling, a part of the* colour was restored (comparison of rate of pseudo-base formation and extent and rate of regeneration of colour-salt). A similar quantitative comparison was made in connexion with the alkali-colour-reactions in aqueous and alcoholic solutions and again no differences could be detected.

The manuscript of this paper was prepared in March and we must now append some preliminary comments on a memoir which appeared on April 11th, in which it is alleged that cyanidin chloride is not 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride.

The evidence on which Malkin and Nierenstein (*Ber.*, 1928, **61**, 797) base this claim is, however, wholly inadequate to sustain their view, as may be seen from a brief analysis of their argument, which runs as follows :

(1) A specimen, X, considered to be 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride, was obtained by the demethylation of its trimethyl ether (Pratt and Robinson). This had certain definite properties; *e.g.*, it gave a pure blue coloration in aqueous solutions having p_H 11·57.

(2) The specimen X differed in many respects from pure cyanidin chloride (Y) derived from cyanin chloride. Malkin and Nierenstein establish this by comparisons described with much circumstantial detail; but here they are forcing an open door, since it is agreed that X and Y as prepared by these authors might exhibit somewhat divergent properties.

(3) Our statement (J., 1927, 1711) that the results of the earlier anthocyanidin syntheses are subject to unexplained variations (hence the necessity for the present communication) was noticed by Malkin and Nierenstein, but they nevertheless considered X to be perfectly homogeneous, chiefly because it was found to be identical with a specimen (Z) synthesised from *O*-triacetylphloroglucinaldehyde and ω : 3 : 4-triacetoxyacetophenone.

This section of the argument is of vital importance, since our

view is that X was not a specimen of a pure pentahydroxyflavylium chloride.

The method of preparation of Z given by Malkin and Nierenstein is based on the process previously used by Nolan, Pratt, and Robinson (J., 1926, 1968) for the syntheses of pelargonidin and peonidin and in the original paper on the latter topics the difficulties experienced in the isolation of the pure salts were emphasised. As stated above, we have tested this synthesis of cyanidin and abandoned it as unsatisfactory. Its use as a method of preparation of a standard is unquestionably an inversion of correct procedure.

A proof of the identify of X and Z is stated to be found in the fact that Z, like X, gives a pure blue coloration at p_H 11·57. We admire the delicacy of perception that enables the p_H of a solution to be determined to one part in a thousand by observation of a change of colour from violet-blue to pure blue. Even if the specimens X and Z were identical, that would not prove that they consisted of pure pentahydroxyflavylium chloride; it would certainly suggest that the impurities have nothing to do with the demethylation and would point to the common factor, namely, the use of *O*-triacetylphloroglucinaldehyde as the starting point (Malkin and Nierenstein state that triacetylphloroglucinaldehyde has m. p. 157°, instead of 151° as recorded by Pratt and Robinson, but they have overlooked the fact that this correction had already been made by the present authors, *loc. cit.*, p. 1713).

The divergences noted as existing between X and Y are not inconsistent with the view that X was an impure specimen of Y except in the one particular that Y gave a good yield of an oxidation product, no trace of which was obtainable from X under the same conditions. This is the only experiment mentioned by Malkin and Nierenstein which has in our opinion a real bearing on the question of the constitution of cyanidin and in this case the details were not disclosed.

After our study of the paper of Malkin and Nierenstein we performed the following experiment. A specimen of cyanidin chloride was prepared from mecocyanin chloride, for the provision of which we are greatly indebted to Professor Willstätter. This was quantitatively compared with our newly synthesised salt (above) and differences, such as those noted by Malkin and Nierenstein as existing between X and Y, could not be detected. The natural and the synthetic specimens gave the same colorations with solutions of definite p_H (6·0, 7·0, 8·0, 9·0, and 10·0) made from the universal buffer solution supplied by the British Drug Houses, Limited. 2 C.c. of a 0·005% alcoholic solution were added to 50 c.c. of the various solutions. As a check, very dilute hydrochloric acid was

added to very dilute aqueous sodium carbonate containing thymolphthalein until the solution became colourless. The p_H should then be 9·0—9·3, and both salts dissolved in this medium to a pure blue solution.

The test with copper sulphate in very dilute solution was repeated under the conditions prescribed by Malkin and Nierenstein with the result that the cyanidin chloride from mecocyanin and our synthetical salt showed an identical behaviour, and it should be observed that this behaviour was similar to that which Malkin and Nierenstein state to be characteristic of natural cyanidin chloride and differed from that of the supposed synthetic pentahydroxyflavylium chloride of these authors.

A sample of cyanidin chloride synthesised by the first method of Pratt and Robinson (J., 1924, **125**, 172) was also examined; it was not quite pure, but its behaviour was so close to that of the cyanidin chloride from mecocyanin that there could be no doubt in regard to the fundamental identity of the substances. Furthermore the description of the salt prepared from trimethylcyanidin by Malkin and Nierenstein does *not* apply to the material obtained in this manner by Pratt and Robinson (J., 1925, **127**, 1189).

Finally, we note that Malkin and Nierenstein have prepared ω-chloro-3 : 4-diacetoxyacetophenone by the interaction of diacetoxybenzoyl chloride and diazomethane. They state that the yellow substance has m. p. 94—95° and have apparently overlooked the already known and convenient method of preparation of this colourless chloro-ketone, which actually melts at 110° * (Voswinckel, *loc. cit.*). It has recently been observed in this laboratory that the interaction of acid chlorides and diazomethane yields the diazoketones, and the case of 3 : 4-diacetoxybenzoyl chloride is no exception. Drs. W. Bradley and G. Schwarzenbach have found that the primary product in this case is ω-diazo-3 : 4-diacetoxyacetophenone, yellow crystals, m. p. 77°, and the details will be published in due course.

The authors wish to express their indebtedness to the Chemical Society and the Royal Society for grants which have defrayed a part of the cost of the investigation.

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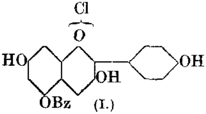
* Dreczgowski (*J. Russ. Phys.-Chem. Soc.*, 1893, **25**, 157) gave the m. p. 95° for this substance, but this was corrected by Voswinckel and we have confirmed the m. p. 110° on several occasions. The m. p. of ω : 3 : 4-triacetoxyacetophenone is 95°.

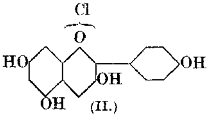
CCI.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XVI. The Synthesis of Pelargonidin Chloride by Means of O-Benzoylphloroglucinaldehyde.*

By ALEXANDER ROBERTSON, ROBERT ROBINSON, and JIRO SUGIURA.

THE condensation of *O*-benzoylphloroglucinaldehyde and ω : 4-diacetoxyacetophenone in ethyl acetate solution in the presence of hydrogen chloride leads to the formation of 3 : 7 : 4′-*trihydroxy-5-benzoyloxyflavylium chloride* (5-O-*benzoylpelargonidin chloride*) (I), which on de-benzoylation is changed to pelargonidin chloride (II).



(I.)



(II.)

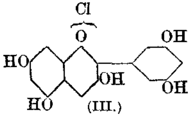
The reactions of (I) resemble those of pelargonenin and pelargonin chlorides, not only in connexion with the colours of acid and alkaline solutions bnt also because the alcoholic solutions exhibit a green fluorescence.

This evidence tends to confirm the view that pelargonenin is a pelargonidin 5- or 7-glucoside. Phloroglucinol derivatives seldom exhibit intense fluorescence, unless in sulphuric acid solution; on the other hand, resorcinol derivatives frequently fluoresce brightly in aqueous or alcoholic solutions and we consider that the presence of the benzoyl group in (I) makes the nucleus virtually equivalent to that of a resorcinol derivative.

The suggestion is that the sugar groups in pelargonenin and pelargonin (also in the *Salvia* series of anthocyanins) exercise a similar function and must therefore he in one of the positions 5 and 7. It should be clearly understood that all remarks in this series of memoirs on the constitution of anthocyanins are based on the assumption that these substances are homogeneous. For example, in regard to pelargonin our definite conclusion is that it is a 5- or 7-diglucoside of pelargonidin *or* that it is a mixture containing sufficient of the 5- or 7-substituted pelargonidin (not necessarily diglucosidoxy-substituted) to enable it to exhibit certain characteristic properties. We consider that pelargonin cannot be pure pelargonidin 3-diglucoside. Naturally it is not possible to express an opinion in regard to this question of the homogeneity of the

anthocyanins without very careful independent examinations, which we have not yet had the opportunity to make in a sufficiently detailed manner.

An account of an attempt to prepare 3 : 5 : 7 : 3′ : 5′-pentahydroxyflavylium chloride (III) is included in this communication. We desired to obtain this salt in order to estimate the importance of the part played by the hydroxyl in position 4′ in determining the reactions of delphinidin.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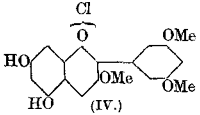
(IV.)

Employing the methods developed in this series of papers, we obtained without difficulty the *trimethyl ether* (IV), but this salt decomposed on attempted demethylation by means of hydriodic acid in the presence of phenol. Indications of the production of (III) were obtained in some experiments.

Experimental.

5-O-*Benzoylpelargonidin Chloride* (I).—A solution of *O*-benzoylphloroglucinaldehyde (7·7 g.) and ω : 4-diacetoxyacetophenone (7·0 g.) in dry ethyl acetate (150 c.c.) was saturated with hydrogen chloride and kept for 3 days. The red crystals that separated were collected (9·5 g.), and a portion was crystallised by solution in the minimnm quantity of cold methyl alcohol and addition of 10% hydrochloric acid until a turbidity appeared. In a few hours microscopic, rectangular plates, having a maroon colour in mass and a deep blue lustre, were deposited (Found in material dried over sulphuric acid and sodium hydroxide: C, 61·0; H, 4·4; Cl, 8·7. $C_{22}H_{15}O_6Cl,1·5H_2O$ requires C, 60·3; H, 4·2; Cl, 8·1%). *Benzoylpelargonidin chloride* dissolves in alcohol to a violet solution and the pseudo-base is formed in very dilute alcoholic solution or on the addition of water. The acid alcoholic solutions resemble aqueous solutions of eosin both in colour and in fluorescence. Aqueous sodium carbonate dissolves the salt to a bright violet solution, but the colour in alcohol, even in 50% alcohol, is pure blue.

Pelargonidin Chloride (II).—Crude benzoylpelargonidin chloride (9·5 g.) was dissolved in a mixture of alcohol (120 c.c.) and 20% aqueous sodium hydroxide (80 c.c.), air being excluded from the apparatus by hydrogen. The intensely purplish-blue solution became dichroic (red) and then green. After 5 hours, concentrated

hydrochloric acid (100 c.c.) was added and the mixture was heated at 60° for a minute, kept for 15 minutes, then cooled, and added to a large volume of ether and 50 c.c. of water. The precipitated salt was collected and washed with 3% hydrochloric acid. The picrate was precipitated from a solution in very dilute hydrochloric acid in crimson needles, which were collected. This material dissolved in ethyl alcohol and immediately separated again; it was redissolved by heating and some picric acid added. The cooled solution deposited short, deep crimson needles. The regenerated chloride separated from the methyl alcohol–ether mixture in swallow-tail-ended leaflets and on recrystallisation, by addition of its filtered solution in methyl alcohol to hot 15% hydrochloric acid, it formed elongated, almost rectangular plates or flat, long prisms (Found: C, 55·8; H, 4·1. Calc. for $C_{15}H_{11}O_5Cl,H_2O$: C, 55·6; H, 4·0%). The salt crystallised from 3% hydrochloric acid in prismatic needles and from methyl alcohol, by exposure of the solution to hydrogen chloride, in sharply cut, almost rectangular, elongated prisms. If a dilute solution of a pure specimen in methyl alcohol is added to hot 15% hydrochloric acid, rhombic plates are obtained and a large proportion of these have broad markings along the diagonals, giving the crystals the appearance of an envelope. Evaporation of a solution in a mixture of ethyl alcohol and 7% hydrochloric acid gave long, flat needles. The substance exhibited *all* the recorded properties of pelargonidin chloride and the only point not checked was the supposed conversion into a new substance by the action of hot *hydrochloric acid*.

When water is added to a concentrated alcoholic solution it is true that a deep red solution is formed and that the colour-base is not precipitated. On long standing, however, a colour-base having a green reflex (duller than that of cyanidin) and a violet colour by transmitted light is deposited. The colour-base is converted into the colour-salt on warming with a dilute solution of tartaric acid or citric acid. The blue solution of pelargonidin in aqueous sodium carbonate is reddish-violet when viewed in the light of a metal-filament lamp.

ω : 3 : 5-*Trimethoxyacetophenone*, $(MeO)_2C_6H_3\cdot CO\cdot CH_2\cdot OMe$.—On methylation by means of methyl sulphate and potassium hydroxide in aqueous methyl-alcoholic solution, orcinol gave a little more than its own weight of the dimethyl ether, b. p. 227—228°/751 mm., and on oxidation by hot 2% aqueous potassium permanganate (twice the theoretical quantity), 3 : 5-dimethoxybenzoic acid, m. p. 181—182° (lit., 180°), was obtained in 25% yield.

Ethyl αγ-dimethoxyacetoacetate (22·8 g.) was gradually added to a suspension of granulated sodium (2·8 g.) in ether (150 c.c.) and when the formation of the sodio-derivative was complete a solution

of 3 : 5-dimethoxybenzoyl chloride (24·1 g.) in ether (95 c.c.) was introduced. The mixture was refluxed for 4 hours and kept for 12 hours. After removal of the solvent the viscous, orange residue was agitated for 12 hours with cold 2·5% aqueous potassium hydroxide (550 c.c.), and the reaction completed by heating on the steam-bath for 4 hours. The neutral product was isolated by means of ether and distilled (6·7 g., b. p. 127—137°/3 mm.). The oil soon solidified and the *ketone* crystallised from light petroleum in colourless needles, m. p. 42° (Found : C, 63·1 ; H, 6·6. $C_{11}H_{14}O_4$ requires C, 62·9; H, 6·7%). The substance is readily soluble in most organic solvents. The *semicarbazone* crystallises from alcohol in colourless needles, m. p. 149—149·5° (Found : N, 16·0. $C_{12}H_{17}O_4N_3$ requires N, 15·7%).

7-Hydroxy-5-benzoyloxy-3 : 3′ : 5′-trimethoxyflavylium Chloride (IV with OBz in position 5).—A mixture of *O*-benzoylphloroglucinaldehyde (2·3 g.), ω : 3 : 5-trimethoxyacetophenone (2·0 g.), and anhydrous ether (500 c.c.) was saturated with hydrogen chloride for a few hours and then kept for 2 days. The brownish-crimson crystals that separated exhibited a green reflex and were collected (0·84 g.). The salt was recrystallised from methyl alcohol containing hydrogen chloride, forming prismatic needles (Found in material dried over sulphuric acid and sodium hydroxide : C, 59·5 ; H, 5·0 ; Cl, 6·9. $C_{25}H_{21}O_7Cl,2H_2O$ requires C, 59·5; H, 5·0; Cl, 7·0%).

5 : 7-Dihydroxy-3 : 3′ : 5′-trimethoxyflavylium Chloride (IV).—(*A*) A *mixture* of ω : 3 : 5-*trimethoxyacetophenone* (3·2 g.), *O*-triacetylphloroglucinaldehyde (4·5 g.), and formic acid (15 c.c.) was cooled and saturated with hydrogen chloride for 3 hours. Next day the product was precipitated by the addition of ether, collected, and hydrolysed by means of boiling alcohol (150 c.c.) and concentrated hydrochloric acid (25 c.c.) for 10 minutes. The greater part of the alcohol was removed by distillation under diminished pressure and 10% hydrochloric acid (100 c.c.) was added to the residue. The crude salt was purified by solution in 0·5% hydrochloric acid and precipitation with concentrated hydrochloric acid and then by crystallisation from methyl alcohol containing hydrogen chloride. The dark violet-brown, flat prisms are reddish-brown by transmitted light and exhibit a coppery glance (Found : C, 58·1 ; H, 5·2; MeO, 22·0. $C_{18}H_{17}O_6Cl,0·5H_2O$ requires C, 58·0; H, 4·8; MeO, 24·4%). In view of the difficulty often experienced in obtaining satisfactory results for methoxyl in the flavylium salt series, the low value found in this case is without significance except that it excludes the composition $C_{18}H_{17}O_6Cl,CH_4O$ (C, 57·6; H, 5·3; MeO, 31·3%). The salt dissolves in aqueous sodium carbonate to a greenish-yellowish-brown solution; it is insoluble in cold 0·5%

hydrochloric acid, but dissolves in the hot solvent to an orange-red solution. The latter gives a dark brownish-violet colour-base on the addition of sodium acetate. The rose-coloured solution in alcohol is decolorised on the addition of water and the colour is rapidly and quantitatively restored on the addition of hydrochloric acid.

(B) The benzoyl derivative (above) was hydrolysed by means of 10% aqueous sodium hydroxide in the absence of air for 4 hours. The regenerated salt was crystallised from dilute hydrochloric acid and then from methyl alcohol containing hydrogen chloride (Found: C, 57·6; H, 5·2%). The salt was identical with that prepared as under (A). All attempts to demethylate this substance and to isolate the product in a pure condition were unsuccessful, but solutions of the pentahydroxyflavylium chloride were probably obtained in the course of the experiments. The bluest alkali-colour-reaction observed was a reddish-purple.

The authors are indebted to the Royal Society for a grant which has defrayed a part of the cost of the investigation.

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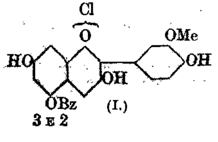
CCII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XVII. The Synthesis of Peonidin Chloride by Means of O-Benzoylphloroglucinaldehyde.*

By SHINZO MURAKAMI and ROBERT ROBINSON.

THE synthesis of peonidin chloride described by Nolan, Pratt, and Robinson (J., 1926, 1968) was a satisfactory proof of the constitution of the anthocyanidin, but the yield was poor and the purification of the salt was difficult to effect.

We have now found that a considerable improvement may be brought about by the substitution of *O*-benzoylphloroglucinaldehyde for the *O*-triacetylphloroglucinaldehyde previously employed.

5-O-*Benzoylpeonidin chloride* (I) is the product of the condensation of *O*-benzoylphloroglucinaldehyde and ω : 4-diacetoxy-3-methoxyacetophenone, $(AcO)(OMe)C_6H_3 \cdot CO \cdot CH_2 \cdot OAc$, by means of hydrogen chloride in ethyl acetate solution.



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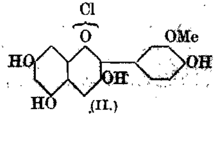

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The hydrates $C_{23}H_{17}O_7Cl,0{\cdot}5H_2O$ and $C_{23}H_{17}O_7Cl,3H_2O$ were isolated and the alkali-colour-reaction of the salt closely resembles that of peonin chloride.

De-benzoylation by the usual method furnished peonidin chloride (II), of which three forms were analysed, namely, $C_{16}H_{13}O_6Cl,H_2O$ and two modifications of the hydrate $C_{16}H_{13}O_6Cl,1{\cdot}5H_2O$. We are very grateful to Professor R. Willstätter for kindly sending us a specimen of peonidin chloride of natural origin (Willstätter and Nolan, *Annalen*, 1915, **408**, 136). A comparison of the reactions of the natural and the synthetic specimen disclosed no differences, but the crystal habit and solubility relations could only be equated after drastic purification of the anthocyanidin from peonin. In the course of work in the flavylium salt group it has frequently been noticed that small traces of persistent impurities completely alter the behaviour of anthocyanidins, and Willstätter and his collaborators have directed attention to this on several occasions.

EXPERIMENTAL.

5-O-Benzoylpeonidin Chloride (I).—A solution of *O*-benzoylphloroglucinaldehyde (2·94 g.) and ω : 4-diacetoxy-3-methoxyacetophenone (2·58 g.) (Nolan, Pratt, and Robinson, *loc. cit.*) in ethyl acetate (75 c.c.) was cooled in running water and saturated with hydrogen chloride. Bright red crystals separated after 2 hours and after being kept over-night the salt was collected, washed with ethyl acetate and ether, and dried in the air (yield, 3·55 g., and 1·22 g. of darker crystalline material by the addition of ether to the mother-liquor) (Found : C, 61·1 ; H, 4·1 ; Cl, 7·3 ; loss at 110° in a vacuum over phosphoric oxide, 2·1. $C_{23}H_{17}O_7Cl,0{\cdot}5H_2O$ requires C, 61·4 ; H, 4·0 ; Cl, 8·0 ; H_2O, 2·0%). The scarlet needles are readily soluble in methyl and ethyl alcohols to crimson solutions that become violet on dilution with more alcohol and colourless on great dilution and warming. The pink colour is quickly and quantitatively regenerated on the addition of hydrochloric acid. Boiling distilled water is not colonred by this salt, which is also very sparingly soluble in hot 0·5% hydrochloric acid. The solution in aqueous *sodium carbonate* is pure blue, greenish-blue in thin layers and purplish-blue in thick layers. The dichroism is barely perceptible by daylight, but by artificial light (metal filament) it is marked and the colour of the solution appears reddish-violet. This contrast has been frequently noticed and it should be understood that all the colorations mentioned in this series of papers have been observed in daylight. Sodium acetate added to an acid alcoholic solution gives a violet coloration and on the addition of water the pseudo-base is quickly formed.

The red crystals (1 g.) were dissolved in methyl alcohol (about 80 c.c.) at 50—60° and warm 15% hydrochloric acid (about 10 c.c.) was added. On keeping short, stout, glistening beetle-green prisms separated; these were yellowish-brown by transmitted light and gave a violet-red smear on paper (Found : C, 56·5; H, 4·7; Cl, 7·3; loss at 160° in a vacuum over phosphoric oxide, 10·9. $C_{23}H_{17}O_7Cl,3H_2O$ requires C, 55·8; H, 4·7; Cl, 7·2; H_2O, 10·9%). The behaviour towards reagents was the same as that of the red crystals.

3 : 5 : 7 : 4′-Tetrahydroxy-3′-methoxyflavylium Chloride (*Peonidin Chloride*) (II).—5-*O*-Benzoylpeonidin chloride (5 g.) was added to 8% aqueous alcoholic (50 c.c. of water and 75 c.c. of alcohol) sodium hydroxide with cooling, and the solution allowed to remain for 3 hours at room temperature; air was excluded by means of nitrogen and the mixture was occasionally shaken. After the addition of concentrated hydrochloric acid (100 c.c.), the whole was heated at 60° for some time and then cooled and kept in the ice-chest for 12 hours. The chocolate-brown precipitate was collected, washed with dilute hydrochloric acid and ether, and dried in the air.

(A). The crude product was dissolved in hot 1% hydrochloric acid, and concentrated hydrochloric acid added so as to bring the concentration of acid to 20%. Crystallisation was rapid and the dark violet product was seen under the microscope to consist of brown, prismatic needles (Found in air-dried material: C, 54·0; H, 4·6; loss at 110° in a vacuum, 4·8. $C_{16}H_{13}O_6Cl,H_2O$ requires C, 54·2; H, 4·2; H_2O, 5·1%). Willstätter and Nolan (*loc. cit.*) crystallised peonidin chloride from 20% hydrochloric acid and found that the product was a monohydrate.

(B). The chocolate-brown crystalline powder separating from 1% hydrochloric acid was dried in the air (Found: C, 52·3; H, 4·5; Cl, 9·9; loss at 110° in a vacuum, 7·4. $C_{16}H_{13}O_6Cl,1{\cdot}5H_2O$ requires C, 52·8; H, 4·4; Cl, 9·8; H_2O, 7·4%).

(C). The crude salt (1 g.) was dissolved in ethyl alcohol (70 c.c.) at 60—70°, and hot 10% hydrochloric acid (20 c.c.) added to the solution. After a few hours, glistening rhombohedra having a brilliant blue reflex separated; the crystals were yellowish-brown when viewed by transmitted light (Found: C, 52·4; H, 4·6; Cl, 9·2; loss at 110° in a vacuum, 7·5%. Theory as above).

The reactions of the three specimens analysed were identical and they were also found to be identical with those of the material of natural origin. The latter was dissolved in 0·5% hydrochloric acid, and the acid concentration brought to 3%. The crystals were collected and converted into the picrate, which was crystallised from a little methyl alcohol. The chloride recovered from the picrate was crystallised from hot dilute hydrochloric acid by bringing

the concentration of hydrogen chloride to 20% and closely resembled our specimen (A) in appearance and crystalline form. A solution of either specimen of the salt (5·0 mg.) in 10 c.c. of alcohol had a bright eosin-red colour tinged with violet; after dilution to 50 c.c., the colour by transmitted light was yellower, duller, and deeper, but thin layers had a bluer cherry-red colour: dilution to 150 c.c. gave a cherry-red solution (S), and 20 c.c. of this diluted to 100 c.c. gave a violet solution the colour of which faded slowly on the addition of an equal volume of water. Addition of sodium acetate to (S) gave a dichroic solution, blue in thin layers, reddish-violet in thick layers, and apparently exhibiting a red fluorescence which is probably an effect of the dichroism. Quantitative colorimetric comparisons showed that at all stages the solutions were identical. Similarly, 5 mg. of each of the specimens were dissolved in 10 c.c. of saturated aqueous sodium carbonate; dilution to 100 c.c. gave a pure blue dichroic solution (violet in thick layers) (T) and dilution to 1000 c.c. gave a greenish-blue solution the dichroism of which was not evident. The two specimens behaved alike and were in this case also compared colorimetrically. The alcoholic solutions (S) gave no coloration on the addition of ferric chloride. A quantitative comparison of the rate of pseudo-base formation and the extent of recovery of pyrylium salt on acidification and heating was also carried out with the result that no differences could be detected. 10 C.c. of a dilute solution of hydrogen peroxide were added to 5 c.c. of the alkaline solutions (T); the colour faded, became green and then yellow, both specimens behaving alike. Many other comparisons were carried out and the only difference noted was that we could not crystallise the specimen of natural origin in the form noted above under (C). We therefore purified it once again through the picrate and the recovered chloride now crystallised from alcohol and 10% hydrochloric acid in more prismatic needles and exhibited a greenish-brown glance. After three more crystallisations a small amount of material of definitely prismatic habit and showing, although in a less well-defined manner, the crystalline form of the specimen (C) and having a green reflex was obtained. We are of the opinion that the anthocyanidins derived from natural sources are sometimes not quite pure and in the case of peonidin the impurity is probably malvidin.

By the addition of a trace of malvidin chloride (synthetic) to the specimen (C) (above) we found that we had obtained a material crystallising under the (C) conditions first indefinitely as a chocolate-brown powder and then in needles, exactly as *natural* peonidin chloride does. Under comparable conditions pure peonidin chloride is much more readily soluble in cold 0·1% hydrochloric acid than in

0·5% hydrochloric acid. The finally purified natural anthocyanidin and the specimen C behaved identically towards these reagents and this was confirmed colorimetrically with the solutions in 0·5% hydrochloric acid.

We desire to thank the Royal Society for a grant which has defrayed a part of the cost of this investigation.

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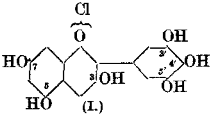
CCCIII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XVIII. A Synthesis of Malvidin Chloride.*

By WILLIAM BRADLEY and ROBERT ROBINSON.

WILLSTÄTTER and MIEG (*Annalen*, 1915, **408**, 122) found that malvin, the anthocyanin of the violet flowers of the wild mallow (*Malva silvestris*, L.), on account of the facility with which its sparingly soluble salts crystallise, could be isolated with particular ease.

Malvin chloride was shown to be the diglucoside of malvidin chloride, itself a dimethyl ether of delphinidin chloride (I), and it is *noteworthy that of the various mono- and di-methyl ethers of*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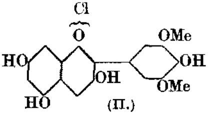
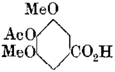

(II.)

delphinidin chloride examined by Willstätter and his collaborators, only malvidin and petunidin gave analytical figures indicating complete homogeneity. The status of malvidin as a chemical individual is unchallenged and it seems probable that petunidin also is a pure substance, namely, delphinidin 3′-methyl ether. Willstätter and Burdick (*Annalen*, 1916, **112**, 217), who isolated and examined petunin chloride, commented on the homogeneity of the pigment and emphasised its importance in connexion with our knowledge of the delphinidin methyl ethers. According to Karrer and Widmer (*Helv. Chim. Acta*, 1927, **10**, 5), however, myrtillidin and œnidin are mixtures containing malvidin, which is evidently one of the more widely distributed anthocyanidins.

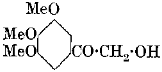
Gatewood and Robinson (Part X, J., 1926, 1959) first suggested that malvidin chloride should be represented by the formula (II),

basing their argument on the reactions of delphinidin chloride 3-methyl ether and of other polyhydroxyflavylium salts related to delphinidin.

Then Anderson and Nabenhauer (*J. Amer. Chem. Soc.*, 1926, **48**, 2997) isolated a pigment from *Isabella* grapes which they considered should be identical with Willstätter and Zollinger's œnin. The related anthocyanidin gave an amorphous product on acetylation, but this was oxidised by potassium permanganate in acetone solution with formation of *O*-acetylsyringic acid (III). This result



(III.)



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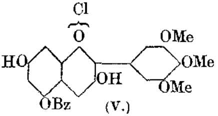


(V.)

could be brought into line with Gatewood and Robinson's view of the constitution of malvidin chloride only on the basis of the hypothesis that specimens of œnidin contain malvidin. A direct proof of the occurrence of the pyrogallol 1 : 3-dimethyl ether group in malvidin was furnished by Karrer and Widmer (*loc. cit.*), who obtained syringic acid by the fission of malvidin with 10% aqueous barium hydroxide and in other ways. These authors propose the name *syringidin* for delphinidin 3′ : 5′-dimethyl ether, but as malvidin is pure syringidin we have retained the name given to the substance by its discoverers, especially since our synthetical material has been identified with the anthocyanidin from malvin chloride.

We take this opportunity of thanking Professor P. Karrer for very kindly supplying specimens of malvin chloride and syringidin chloride which have greatly assisted us in this investigation. The methods that have been devised for the preparation of the benzoylcarbinol derivatives required for the synthesis of other anthocyanidins are not applicable to the intermediate for malvidin, chiefly because the Friedel–Crafts and analogous reactions applied to pyrogallol ethers lead to the formation of 4-acyl derivatives having the type of orientation characteristic of pyrogallolcarboxylic acid rather than of gallic acid. We therefore decided to seek a method of effecting the change $R\cdot CO_2H \longrightarrow R\cdot CO\cdot CH_2\cdot OH$ which could be used when gallic acid or one of its derivatives was the point of departure. Direct halogenation of acetophenone derivatives could not be employed in this instance because of the ease with which the aromatic nucleus was attacked by the reagent and for one reason or another none of the more obvious methods could be utilised.

However, an observation of Raper and Clutterbuck (*Biochem. J.*,

1926, **20**, 63), that hydroxyacetoacetic acid and acetol are among the products of oxidation of ethyl acetoacetate by hydrogen peroxide in the presence of alkalis, suggested an application to the preparation of benzoylcarbinols, and we developed our attack of this problem in this direction in the first instance. The action of hydrogen peroxide on ethyl 3 : 4 : 5-trimethoxybenzoylacetate and 3 : 4 : 5-*trimethoxydibenzoylmethane* in the presence of sodium hydroxide gave rise to substances which reduced Fehling's solution in the cold, but use could not be made of the reaction as a method of preparing trimethoxybenzoylcarbinol. It was desirable to introduce a modification in which the use of aqueous solutions could be avoided and the hydroxyl group could be protected.

These requirements are fulfilled by a method depending on the interaction of acyl peroxides and the sodium derivatives of β-ketonic esters in benzene suspension. The reaction proceeds in accordance with the equation $R{\cdot}CO{\cdot}CH{\cdot}CO_2Et\}Na + X_2(CO{\cdot}O)_2 = R{\cdot}CO{\cdot}CH(O{\cdot}COX){\cdot}CO_2Et + X{\cdot}CO_2\}Na$. Ethyl benzoylacetate and benzoyl peroxide gave, in this way, *ethyl benzoylbenzoyloxyacetate*, $COPh{\cdot}CH(O{\cdot}COPh){\cdot}CO_2Et$ (VI), in satisfactory yield; difficulties were, however, encountered in attempting the hydrolysis of this ester. Ultimately it was found that phenacyl benzoate,

$$COPh{\cdot}CH_2{\cdot}O{\cdot}COPh,$$

could be obtained from it by heating with water in a sealed tube at 200°, but further degradation to benzoylcarbinol could only be accomplished in poor yield by means of boiling aqueous-alcoholic sulphuric acid. Zincke (*Annalen*, 1883, **216**, 308) was unable to obtain benzoylcarbinol by the hydrolysis of its benzoate.

Similarly, the sodio-derivative of ethyl 3 : 4 : 5-trimethoxybenzoylacetate and benzoyl peroxide furnished *ethyl* 3 : 4 : 5-*trimethoxybenzoylbenzoyloxyacetate*, $C_6H_2(MeO)_3{\cdot}CO{\cdot}CH(O{\cdot}COPh){\cdot}CO_2Et$ (VII), and ω-*benzoyloxy*-3 : 4 : 5-*trimethoxyacetophenone*,

$$C_6H_2(MeO)_3{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}COPh \text{ (VIII)},$$

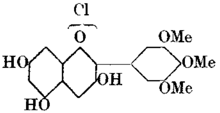
but the latter could neither be condensed with *O*-benzoylphloroglucinaldehyde to a flavylium salt nor hydrolysed to trimethoxybenzoylcarbinol. In view of the fact that the hydrolysis of phenacyl acetate presents little difficulty, we next substituted acetyl peroxide for benzoyl peroxide and thus obtained *ethyl* 3 : 4 : 5-*trimethoxybenzoylacetoxyacetate*,

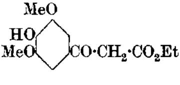
$$C_6H_2(MeO)_3{\cdot}CO{\cdot}CH(OAc){\cdot}CO_2Et \text{ (IX)},$$

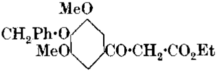
and by direct hydrolysis with hot dilute sulphuric acid, 3 : 4 : 5-*trimethoxybenzoylcarbinol* (IV).

This ketone condensed very readily with *O*-benzoylphloroglucinaldehyde (Robertson and Robinson, J., 1927, 1710) to give 3 : 7-*dihydroxy*-5-*benzoyloxy*-3′ : 4′ : 5′-*trimethoxyflavylium chloride*

(V), which was converted by the successive action of cold aqueous sodium hydroxide and hydrochloric acid into delphinidin chloride 3′ : 4′ : 5′-trimethyl ether (X), a methyl ether of malvidin chloride (II). A comparison of the reactions of (X) with those of malvidin

(X.) 

 (XIII.)

 (XIV.)

serves to confirm the view, first put forward by Heilbron, that a pure blue alkali-colour-reaction in the anthocyanin series is associated with a free hydroxyl group in position 4′. Since the partial hydrolysis of pyrogallol trimethyl ether and of gallic acid trimethyl ether affords pyrogallol 1 : 3-dimethyl ether and syringic acid, respectively, we concluded that it might be possible to hydrolyse (X) to malvidin. A product having most of the properties of this anthocyanidin, and doubtless containing it in preponderating amount, was obtained from the trimethyl ether by the action of hydrogen bromide in acetic acid solution at 45—50°. This material was contaminated with delphinidin or, more probably, delphinidin 3′-methyl ether, since it exhibited a ferric chloride reaction. By taking advantage of the sparing solubility of malvidin sulphate, a small pure specimen of the salt was isolated and this exhibited the colour reactions characteristic of the natural anthocyanidin.

In any case, this synthesis suffers from the defect that it does not determine the constitution of the product, but merely limits it to one of two alternatives, and we therefore turned our attention to a method free from such ambiguity.

O-*Acetylsyringoyl chloride*, $C_6H_2(OAc)(OMe)_2{\cdot}COCl$ (XI), and ethyl sodioacetoacetate gave rise to *ethyl acetylsyringoylacetoacetate*, $C_6H_2(OAc)(OMe)_2{\cdot}CO{\cdot}CHAc{\cdot}CO_2Et$ (XII), and this on hydrolysis yielded *ethyl syringoylacetate* (XIII). These esters could not be transformed into acyloxy-derivatives.

Ethyl O-*benzylsyringoylacetate* (XIV) was therefore prepared by condensing O-*benzylsyringoyl chloride*, $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}COCl$ (XV), with ethyl sodioacetoacetate and hydrolysing the product, and this ester could be oxidised normally by means of benzoyl peroxide. The primary product could not be purified, but on hydrolysis it yielded *ω-benzoyloxy-4-benzyloxy-3 : 5-dimethoxyaceto-*

phenone, $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH_2{\cdot}O{\cdot}COPh$ (XVI), which, however, like other ω-benzoyloxyacetophenone derivatives, did not condense readily with *O*-benzoylphloroglucinaldehyde to a flavylium salt. A small quantity of a by-product was once obtained in the course of the preparation of (XVI), and this was doubtless *benzylsyringoylcarbinol*, $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH_2{\cdot}OH$ (XVII), since it reduced Fehling's solution in the cold and condensed with *O*-benzoylphloroglucinaldehyde to a salt which, in the light of later experience, we regarded as benzoylmalvidin chloride.

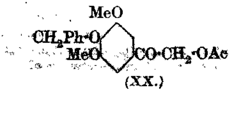
Under conditions similar to those which we were able to employ in the case of trimethoxybenzoylacetic ester the interaction of ethyl sodiobenzylsyringoylacetate and acetyl peroxide would without doubt proceed smoothly. These conditions, however, involve the handling of solid acetyl peroxide, which is capriciously and dangerously explosive. At this stage one of us had an unpleasant experience, a quantity of the peroxide exploding with extreme violence without any apparent cause that can be recalled. When it was possible to resume these experiments the use of the crystallised reagent was barred, but unfortunately the employment of the crude peroxide in solution never gave entirely satisfactory results. These are described in the experimental section (p. 1558).

Oxidation of ethyl benzylsyringoylacetate (XIV) by means of lead tetra-acetate in acetic acid solution gave *ethyl di(benzylsyringoyl) succinate*, $[CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH(CO_2Et){\cdot}]_2$ (XVIII), which was also obtained by the action of iodine on the potassium derivative of (XIV).

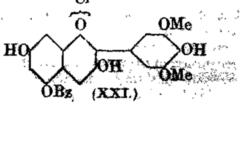
Apart from the use of pure acetyl peroxide, these oxidation experiments gave us little hope of a successful outcome and we therefore turned our attention to a method developed by Nierenstein. According to this author the action of diazomethane on acid chlorides is to produce related ω-chloro-ketones :

$$R{\cdot}COCl + CH_2N_2 \longrightarrow R{\cdot}CO{\cdot}CH_2Cl + N_2.$$

The interaction of diazomethane and benzylsyringoyl chloride (XV) in ethereal solution gave rise, however, to *ω-diazo-4-benzyloxy-3 : 5-dimethoxyacetophenone*, $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CHN_2$ (XIX) in excellent yield. When this was warmed with acetic acid, nitrogen was readily evolved and *ω-acetoxy-4-benzyloxy-3 : 5-dimethoxyacetophenone* (XX) was produced.



(XX.)



(XXI.)

We have recently shown that benzoyl chloride and diazomethane yield diazoacetophenone and our further work has confirmed the general character of the reaction, which has a wide scope as a synthetic method.* The condensation of *O*-benzoylphloroglucinaldehyde with (XX) in cold ethyl acetate solution by means of hydrogen chloride yields benzoylmalvidin chloride (XXI), the acetoxy- and benzyloxy-groups being hydrolysed. The alkali-colour-reaction of this 5-benzoylmalvidin chloride closely resembles that of malvin chloride. De-benzoylation was effected by means of cold aqueous sodium hydroxide and subsequent treatment with hydrochloric acid reconstructed the pyrylium ring broken by the alkali. The product (II) had all the characteristic properties and reactions of malvidin chloride as described by Willstätter and Mieg (*loc. cit.*) and careful comparison with a specimen obtained by the hydrolysis of natural malvin chloride showed that the two were identical.

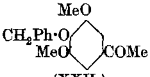
Certain flavylium salts closely related to malvidin chloride have also been synthesised with the object of eliciting further evidence in regard to the constitution of malvin chloride. The results indicate that malvin is a malvidin 5- or 7-diglucoside, whereas Karrer and Widmer (*Helv. Chim. Acta*, 1927, **10**, 729) consider it to be malvidin 3-diglucoside. If the methylation experiments of Karrer and Widmer may be interpreted in the manner suggested by Robertson and Robinson (this vol., p. 1463), the 7-diglucoside configuration can be excluded and malvin should be the 5-diglucoside of malvidin.

Briefly our argument is that a free hydroxyl group not only in position 4′ but also in position 3 is essential for the exhibition of a pure greenish-blue alkali-colour-reaction in the malvidin series; 3-des-hydroxymalvidin and malvidin 3-methyl ether give alkali-colour-reactions divergent from those of malvin, malvidin, and 5-benzoylmalvidin. It might be objected that the effects of the methoxyl and diglucosidoxyl groups in position 3 on the colour reaction might be very different, but there is evidence that this is

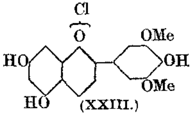
* (*Added, June 9th.*) Arndt, Eistert, and Partale (*Ber.*, 1927, **60**, 1364) found that the interaction of *o*-nitrobenzoyl chloride and diazomethane gave a compound $C_8H_5O_3N_3$ which they suggested might be ω-diazo-*o*-nitroacetophenone. Simultaneously with the present authors, Arndt and Amende (*Ber.*, 1928, **61**, 1222) showed that benzoyl chloride and diazomethane yield diazoacetophenone, and the German chemists also prepared diazoacetone and diazochloroacetone analogously. Arndt and his colleagues have been hampered by the effort to accommodate the contrary results of Dale and Nierenstein (*Ber.*, 1927, **60**, 1026) and this accounts for their provisional recognition of the substance $C_8H_5O_3N_3$ as diazonitroacetophenone; it is clear, however, that they were the first to offer a correct interpretation of the reaction between an acid chloride and diazomethane.

not the case. In the first place the diglucosides have the same alkali-colour-reactions as the monoglucosides to which they give rise on step-wise hydrolysis. For instance, Willstätter and Bolton (*Annalen*, 1916, **412**, 136) found that pelargonenin (pelargonidin monoglucoside) had almost the same reactions as pelargonin (pelargonidin diglucoside); chrysanthemin (cyanidin monoglucoside) and mecocyanin (cyanidin diglucoside) provide a further example. Secondly Robertson and Robinson have prepared pelargonidin 3-methyl ether (J., 1927, 1715) and pelargonidin 3-glucoside (this vol., p. 1460), and the alkali-colour-reactions of these substances closely resemble one another.

Ethyl *O*-benzylsyringoylacetate (XIV) was hydrolysed by means of water at 175—180° with formation of *4-benzyloxy-3 : 5-dimethoxyacetophenone* (XXII). This ketone condenses with *O*-benzoylphloroglucinaldehyde in ethyl acetate solution in the presence of hydrogen chloride to produce what is apparently a mixture of the anticipated flavylium salt with a de-benzylated derivative. On complete de-benzoylation and de-benzylation, pure *5 : 7 : 4'-trihydroxy-3' : 5'-dimethoxyflavylium chloride* (XXIII) was obtained.



(XXII.)



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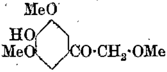
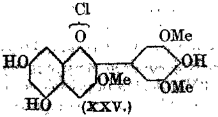
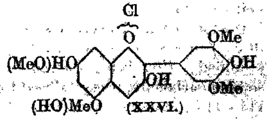


(XXIV.)

O-Acetylsyringoyl chloride reacted with ethyl sodio-αγ-dimethoxyacetoacetate (Pratt and Robinson, J., 1925, **127**, 168) to form a product which on hydrolysis afforded *4-hydroxy-ω : 3 : 5-trimethoxyacetophenone* (XXIV). This ketone condensed normally with *O*-benzoylphloroglucinaldehyde and hydrogen chloride to give *7 : 4'-dihydroxy-5-benzoyloxy-3 : 3' : 5'-trimethoxyflavylium chloride*, and on debenzoylation *5 : 7 : 4'-trihydroxy-3 : 3' : 5'-trimethoxyflavylium chloride* (XXV) could be isolated.



(XXV.)



(XXVI.)

This malvidin 3-methyl ether is isomeric with hirsutidin, a new anthocyanidin obtained by Karrer and Widmer (*Helv. Chim. Acta*, 1927, **10**, 758) from the diglucosidic anthocyanin of *Primula hirsuta*. The presence of the syringic acid group in hirsutin was demonstrated by Karrer and Widmer and since the carbohydrate residues in malvin and hirsutin were supposed to be attached to position 3, these authors considered that hirsutidin must have one of the constitutions represented by (XXVI). The reactions of (XXV) show that it is not identical with hirsutidin and therefore from a different point of view we confirm the conclusions of Karrer and Widmer in regard to the constitution of this anthocyanidin.

Experimental.

Ethyl Benzoylbenzoyloxyacetate (VI).—The action of benzoyl peroxide (1 mol.) on ethyl sodioacetoacetate (1 mol.) gave rise to sodium benzoate (1 mol.) and an oil containing only a trace of ethyl acetoacetate. This was doubtless ethyl benzoyloxyacetoacetate, but as it did not crystallise the further investigation of the reaction was postponed.

Benzoyl peroxide (12·1 g.; m. p. 106° with decomp.), dissolved in benzene (130 c.c.), was added in four portions at intervals of 10 minutes to ethyl sodiobenzoylacetate (from 9·6 g. of the ester and 1·15 g. of sodium powder) in ethereal suspension and solution at 0°. After a short time an aqueous extract of the ethereal solution was neutral and this indicated the completion of the reaction. The prodnct was isolated by the addition of water and subsequent washing of the benzene solution (5·2 g. of benzoic acid were obtained on evaporation and acidification of the aqueous solutions), which was dried and evaporated. The residue crystallised in contact with light petroleum and the substance was twice recrystallised from the same solvent, forming rosettes of slender, colourless prisms, m. p. 61° (Found: C, 69·1; H, 5·0. $C_{18}H_{16}O_5$ requires C, 69·0; H, 5·0%).

Ethyl benzoylbenzoyloxyacetate is readily soluble in cold methyl alcohol and benzene and sparingly soluble in light petroleum. It slowly reduces Fehling's solution in the cold. Its alcoholic solution gives no coloration with ferric chloride, and no copper derivative could be isolated. Moreover the ester is considerably more difficult to hydrolyse to a related ketone than is ethyl benzoylacetate, neither acid nor alkaline catalysts being effective: the best process is the following. The crude substance (9 g.) was heated with water (9 c.c.) in a sealed tube at 200° for 2 hours. On cooling, the oil solidified; after being washed in ethereal solution with aqueous sodium carbonate, it crystallised from 95% alcohol in prisms, m. p. 114—115°, identified as ω-benzoyloxyacetophenone by comparison

with the product obtained from silver benzoate and ω-bromoacetophenone.

A mixture of ω-benzoyloxyacetophenone (6 g.), sulphuric acid (10 g.), water (20 c.c.), and enough alcohol to give a clear solution was refluxed for 12 hours. From the product, benzoylcarbinol was isolated in unsatisfactory yield; it had m. p. 71—73° after crystallisation from aqueous alcohol and reduced Fehling's solution in the cold.

Ethyl 3 : 4 : 5-*Trimethoxybenzoylacetate*,

$$C_6H_2(MeO)_3\cdot CO\cdot CH_2\cdot CO_2Et.$$

—This ester has been obtained by Perkin and Weizmann (J., 1906, **89**, 1655) and by Mauthner (*J. pr. Chem.*, 1910, **82**, 278). The following modification of Perkin and Weizmann's method gave good results.

Gallic acid (150 g., crystallised) gave 120—130 g. of the trimethyl ether, m. p. 163—164°, or 100—110 g. of material, m. p. 168° (Graebe and Martz, *Annalen*, 1905, **340**, 219; Bogert and Isham, *J. Amer. Chem. Soc.*, 1914, **36**, 514). A solution of sodium ethoxide (from 16·1 g. of sodium) in alcohol (270 c.c.) was prepared and 135 c.c. of this were added to a mixture of ethyl acetoacetate (47·5 g.) and ether (280 c.c.) cooled in ice. When the temperature had fallen below 2°, a suspension of finely powdered 3 : 4 : 5-trimethoxybenzoyl chloride (40 g. of distilled material, b. p. 183—185°/18 mm., m. p. 76—78°) in ether (100 c.c.) was added in three portions with vigorous shaking. After 1 hour, the reaction appeared to be finished and further quantities of the sodium ethoxide solution (65 c.c., 33 c.c., 17 c.c., remainder) and of trimethoxybenzoyl chloride (20·2 g., 10·2 g., 5·1 g., and 5·0 g.) suspended in ether were added alternately and under the same conditions as before. After 12 hours, the precipitate was collected, washed with ether, and mixed with crushed ice, and the whole was acidified with dilute hydrochloric acid. The crystalline product (125 g.) was isolated by means of ether. It was hydrolysed in portions of 41 g. by mixing it with water (1000 c.c.) and ammonium chloride (70 g.) and adding concentrated aqueous ammonia (175 c.c.). The clear yellow solution deposited ethyl 3 : 4 : 5-trimethoxybenzoylacetate, which crystallised from methyl alcohol in colourless plates, m. p. 94—95° (total yield, 54 g.).

Ethyl 3 : 4 : 5-*Trimethoxybenzoylbenzoyloxyacetate* (VII).—In the preparation of this substance the use of potassium in place of sodium had a double advantage; the metal could be pulverised under benzene and the formation of the sodium derivative of the ester was found to be very slow. Ethyl 3 : 4 : 5-trimethoxybenzoylacetate (42 g.), dissolved in benzene (100 c.c.), was added to potassium powder (5·8 g.) and benzene (100 c.c.). A gentle reaction ensued

and the potassium derivative separated. After 15 minutes the semi-solid mass was heated on the steam-bath until the evolution of hydrogen ceased and then cooled in ice during the gradual addition of a solution of benzoyl peroxide (36 g.) in benzene (400 c.c.). When an aqueous extract was neutral in reaction, water was added, the benzene layer was washed and dried, and the solvent was removed. The pale yellow residue crystallised in contact with methyl alcohol and on recrystallisation from the same solvent formed colourless rhombs, m. p. 107° (Found: C, 62·8; H, 5·4. $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%). The yield of material, m. p. 106—107°, was 39 g., and a further quantity (5—6 g.) was obtained from the mother-liquors.

The ester is readily soluble in most organic solvents and gives no coloration with alcoholic ferric chloride. It reduces Fehling's solution on warming and dissolves in sulphuric acid to an orange-yellow solution.

This ester is much more stable to hydrolysing agents than ethyl benzoylbenzoyloxyacetate (above). After heating with water at 200° for 4 hours, unchanged substance, m. p. 105—107°, was recovered (Found: C, 62·6; H, 5·8%). Neither alkaline nor acid agents could be employed to effect the hydrolysis.

ω-*Benzoyloxy*-3 : 4 : 5-*trimethoxyacetophenone* (VIII).—A mixture of the foregoing ester (10 g.) and water (6 c.c.) was heated in a sealed tube at 200° for 14 hours. On cooling, a little benzoic acid separated; the aqueous solution strongly reduced Fehling's solution in the cold. The pale brown oil crystallised in contact with methyl alcohol. A solution of it in ether was washed with aqueous sodium carbonate, dried, and concentrated to 15—20 c.c. The crystals that separated were recrystallised from methyl alcohol; faintly yellow parallelepipeds, m. p. 98—100°, were obtained, and colourless needles, m. p. 97—100°, from the mother-liquor. The mixture had m. p. 97—100° and when the prisms were recrystallised the m. p. 98—100° was unchanged and again colourless needles separated from the mother-liquor (Found: C, 65·3; H, 5·2. $C_{18}H_{18}O_6$ requires C, 65·4; H, 5·5%). The substance dissolves in sulphuric acid to a bright yellow solution. It does not reduce Fehling's solution in the cold, but does so rapidly on heating. Hydrolysis of this substance by means of alkaline solutions yielded only benzoic and trimethoxybenzoic acids, and on treatment with aqueous-alcoholic sulphuric acid it (3 g.) gave only 0·1—0·2 g. of the carbinol. It is remarkable that ω-benzoyloxytrimethoxyacetophenone exhibited scarcely any tendency to condense with *O*-benzoylphloroglucinaldehyde to a flavylium salt.

Ethyl 3 : 4 : 5-*Trimethoxybenzoylacetoxyacetate* (IX).—Acetyl peroxide was prepared by the method of Clover and Richmond (*Amer.*

Chem. J., 1903, **29**, 182); 40 g. of acetic anhydride gave 10—11 g., m. p. 27—29°. The instability of this substance renders it unsuitable for general use in the absence of special precautions.

Ethyl 3 : 4 : 5-trimethoxybenzoylacetate (8·0 g.) was converted into its potassium derivative (1·1 g. of potassium powder) in benzene, and to this, cooled in ice, acetyl peroxide (3·2 g.) dissolved in a little benzene was added in one portion. The reaction was still incomplete after 4 hours, and the mixture was heated at 30—40° for 1 hour; an aqueous extract then had a neutral reaction. Water was added and the benzene layer was washed, dried, and evaporated, leaving a residue which was crystallised from methyl alcohol. The yield was 4·5 g., m. p. 85—87°, and 3·5 g. of a somewhat less pure material were obtained from the mother-liquor.

Ethyl trimethoxybenzoylacetoxyacetate is sparingly soluble in light petroleum but readily soluble in benzene and methyl alcohol, from which it crystallises in colourless prisms, m. p. 88° (Found : C, 56·4; H, 5·7. $C_{16}H_{20}O_8$ requires C, 56·4; H, 5·9%). The reactions of the ester resemble those of the corresponding benzoyloxy-derivative, from which it is distinguished by its much more ready reduction of Fehling's solution and by its capacity for hydrolysis to trimethoxybenzoylcarbinol.

*ω-Hydroxy-*3 : 4 : 5*-trimethoxyacetophenone* (IV).—Ethyl trimethoxybenzoylacetoxyacetate (2·2 g.) was hydrolysed by boiling 10% sulphuric acid for 3 hours. A portion of the product (0·4 g.) separated on cooling and an equal amount was isolated by means of ether. The *keto-alcohol* crystallised from benzene–light petroleum in long, colourless needles, m. p. 87—88° (Found : C, 58·1; H, 6·7. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%). This substance is readily soluble in alcohol and benzene and moderately readily soluble in water; cold Fehling's solution is rapidly reduced. The *diphenylhydrazone* of 3 : 4 : 5*-trimethoxyphenylglyoxal*, obtained in dilute acetic acid solution, crystallised from aqueous pyridine in stellate clusters of serrated, yellow plates, m. p. 137—138°. The *carbinol* obtained as mentioned above from ω-benzoyloxy-3 : 4 : 5-trimethoxyacetophenone was identified by conversion into this derivative.

3 : 5 : 7*-Trihydroxy-*3′ : 4′ : 5′*-trimethoxyflavylium Chloride* (X).—A solution of ω-hydroxy-3 : 4 : 5-trimethoxyacetophenone (0·77 g.) and *O*-benzoylphloroglucinaldehyde (0·87 g.) in absolute ether was cooled in melting ice and saturated with hydrogen chloride. After 3 hours the product was isolated (0·44 g.) as a maroon powder exhibiting a greenish-yellow lustre. The salt crystallised from aqueous-alcoholic hydrochloric acid in crimson needles; it was readily soluble in methyl alcohol, less readily in ethyl alcohol, to

crimson solutions tinged with violet. On dilution, the pseudo-base was readily formed and the colour was restored by the addition of hydrochloric acid.

When this dihydroxybenzoyloxytrimethoxyflavylium chloride (0·32 g.) was dissolved in cold 10% aqueous sodium hydroxide (3 c.c.), air being excluded by hydrogen, the violet solution became red and then deep orange. After 6 hours, a buff-coloured solid was precipitated by the addition of water and concentrated hydrochloric acid (2 c.c.) and on heating a crimson colour developed and soon the pyrylium salt separated in hair-like needles. This delphinidin chloride trimethyl ether crystallised from aqueous-alcoholic hydrochloric acid in deep red, elongated prisms (Found : C, 54·4; H, 4·8. Calc. for $C_{18}H_{17}O_7Cl,H_2O$: C, 54·2; H, 4·8%).

In mass, this salt has a deep crimson-brown colour and a yellow lustre; it is readily soluble in alcohol and moderately readily soluble in dilute hydrochloric acid to bluish-red solutions. The red amyl-alcoholic extract from acid aqueous solutions becomes violet-red on the addition of sodium acetate, and the solution in aqueous sodium carbonate is strongly dichroic, being crimson in thick layers and bluish-violet in thin layers.

Acetic acid (3 c.c.) was saturated with hydrogen bromide at 60° and cooled, and 3 : 5 : 7-trihydroxy-3′ : 4′ : 5′-trimethoxyflavylium chloride (0·1 g.) added; when the temperature was slowly raised to 45—50°, the salt dissolved completely to a clear red solution. The colour developed on the addition of a drop of the liquid to aqueous sodium carbonate was tested at frequent intervals and even after a few minutes the pure blue malvidin reaction was observed. After 10 minutes, the liquid was cooled and a portion crystallised; less satisfactory material was obtained on dilution of the mother-liquor with water. The purer fraction had many of the properties of a malvidin salt, but it gave a ferric chloride reaction and was therefore contaminated with delphinidin or more probably a delphinidin monomethyl ether. It was dissolved in a little 0·5% hydrochloric acid, and 7% sulphuric acid added so as to give a 2% concentration of sulphuric acid; the process was repeated with the brown deposit obtained after a few hours' keeping. A very small quantity of a sulphate giving a pure blue alkali-colour-reaction and a very weak ferric chloride reaction was thus isolated. This was undoubtedly crude malvidin sulphate, but the process was not satisfactory and a synthesis of a more precise nature was undertaken. The experience gained was, however, valuable, since it was learned that the methoxyl in position 4′ is preferentially attacked by acids.

O-*Acetylsyringoyl Chloride* (XI).—The method for the preparation

of syringic acid indicated by Alimanchandi and Meldrum (J., 1920, **117**, 967) was not described in sufficient detail to permit of repetition. The following conditions gave consistent results (yield, about 80%). A solution of 3 : 4 : 5-trimethoxybenzoic acid (23 g.) in 96—98% sulphuric acid (92 c.c.) was heated at 50° for 6 hours and then added to water (200 c.c.). The silky needles, m. p. 199—201°, obtained were recrystallised from water and then melted at 205° (yield, 17 g.; methyl ester, m. p. 85°). Syringic acid was also prepared by the method of Bogert and Isham (*J. Amer. Chem. Soc.*, 1914, **36**, 519) as improved by Bogert and Ehrlich (*ibid.*, 1919, **41**, 798) and in this process we found it very important to use gallic acid trimethyl ether of m. p. not lower than 163—164°.

Syringic acid may be acetylated by boiling with an excess of acetic anhydride for 4 hours, or in a shorter period of heating on the steam-bath if zinc chloride or pyridine is employed as a catalyst; the latter method gave a 92% yield of material of m. p. 186°. After several crystallisations from benzene the m. p. remained constant at 187° (Found: C, 54·8; H, 5·0. Calc. for $C_{11}H_{12}O_6$: C, 55·0; H, 5·0%). Anderson and Nabenhauer (*J. Amer. Chem. Soc.*, 1926, **48**, 2997) give the m. p. 190°.

The *chloride* was obtained by means of phosphorus pentachloride, acetyl chloride or benzene being used as a diluent. (1) *O*-Acetylsyringic acid (12 g.) was covered with acetyl chloride (15 c.c.), and phosphorus pentachloride (12 g.) gradually added; the reaction was completed by gentle heating for 1 hour and, on keeping, the chloride crystallised in prisms. It was recrystallised from benzene–light petroleum, forming long, colourless prisms, m. p. 126° (Found: C, 51·2; H, 4·4. $C_{11}H_{11}O_5Cl$ requires C, 51·1; H, 4·3%). The yield was 7 g. A further quantity (2 g.) was obtained from the mother-liquor. (2) The acid (50 g.) and phosphorus pentachloride (45 g.) in benzene (30 c.c.), heated in the steam-bath for only 10 minutes, gave a crude product (33 g.), m. p. 114—120° (after one recrystallisation, the chloride had m. p. 121—123° and was sufficiently pure for most purposes), and a further 9 g. were obtained from the mother-liquor. The reaction could also be carried out in the cold in 5 hours, about 4 times the volume of benzene here prescribed being used; the product, m. p. 123—124°, was purer, but the yield was smaller.

Ethyl O-*Acetylsyringoylacetoacetate* (XII).—A solution (80 c.c.) of sodium methoxide (6·9 g. of sodium) in methyl alcohol was prepared and half of it was added to a mixture of ethyl acetoacetate (19·5 g.) and ether (60 c.c.) cooled in ice. A suspension of powdered acetylsyringoyl chloride (19·5 g.) in ether (50 c.c.) was then introduced in three portions with vigorous shaking. Further additions of the

sodium methoxide solution (20 c.c., 10 c.c., 5 c.c., remainder) and of acetylsyringoyl chloride (9·75 g., 4·9 g., 2·45 g., 2·4 g.) were then made alternately. Next day the salts were collected, washed with ether, and added to ice-cold dilute hydrochloric acid; the new ester was then precipitated and quickly crystallised. It was recrystallised from methyl alcohol (yield, 23 g.; m. p. 112—114°); the pure *substance* separated in glistening, colourless leaflets or elongated plates, m. p. 114° (Found: C, 58·3; H, 5·8. $C_{17}H_{20}O_8$ requires C, 58·0; H, 5·7%). The analysis does not exclude the possibility that the substance is ethyl syringoylacetoacetate ($C_{15}H_{18}O_7$ requires C, 58·1; H, 5·8%). It is soluble in aqueous sodium carbonate to a pale yellow solution, and a red coloration is developed on the addition of ferric chloride to its alcoholic solution. The substance described in the next section gives an abnormal ferric chloride reaction, probably on account of the presence of the phenolic hydroxyl in the benzene nucleus, and therefore the normal behaviour of the ester now under discussion is evidence in favour of the constitution (XII).

Ethyl Syringoylacetate (XIII).—Finely powdered ethyl acetylsyringoylacetoacetate (12 g.) was added to a mixture of water (250 c.c.), concentrated aqueous ammonia (15 c.c.), and ammonium chloride (20 g.). Within a few minutes, the ester dissolved to a yellow solution, from which a new substance quickly separated (an aqueous solution of this yielded ethyl syringoylacetate on acidification); after 30 minutes, the colourless solution was acidified, and the product collected (8·5 g.). The *ester* crystallised from methyl alcohol in slender, colourless prisms or rods, m. p. 92° (Found: C, 58·4; H, 6·0. $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0%). Again analysis does not exclude the formula $C_{15}H_{18}O_7$.

The substance crystallises from hot water in colourless prisms; it is moderately readily soluble in ether and very readily soluble in alcohol or benzene. It gives with ferric chloride in alcoholic solution a bright emerald-green coloration, which changes quickly through olive to brownish-red. The association of this curious reaction with the presence of the phenolic group was confirmed by the observation that Schotten–Baumann benzoylation of the ester furnished a product that gave a crimson coloration with ferric chloride in alcoholic solution. The addition of copper acetate to an aqueous solution of the ester gave an insoluble brown copper salt, and this behaviour also is suggestive of the presence of a free phenolic hydroxyl group.

Experiments on the acetoxylation of ethyl syringoylacetate and ethyl acetylsyringoylacetoacetate through the interaction of their sodium salts with acetyl peroxide gave small quantities of reducing substances, but the yields were uniformly inadequate.

Mr. Leslie R. Ridgway, M.Sc., collaborated with us in the preparation of the derivatives of syringic acid described above.

Methyl 4-Benzyloxy-3 : 5-dimethoxybenzoate (*Methyl O-Benzylsyringate*), $CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO_2Me$.—A solution of potassium hydroxide (11·2 g.) in methyl alcohol (100 c.c.) was added to one of methyl syringate (46 g.) and benzyl chloride (25·3 g.) in methyl alcohol (50 c.c.); the potassium salt crystallised. The mixture was boiled for 5 hours, the reaction then being neutral, and the filtered solution on cooling deposited elongated prisms (35 g.); a further quantity was obtained from the mother-liquor. The *ester* crystallised from 95% alcohol (yield, 38 g.; m. p. 69—71°) in pointed, hexagonal prisms, m. p. 71° (Found: C, 67·3; H, 5·9. $C_{17}H_{18}O_5$ requires C, 67·5; H, 6·0%). It is readily soluble in most organic solvents; its bright yellow solution in concentrated sulphuric acid changes rapidly through emerald-green to bluish-green. Attempts to prepare (XIV) by condensing this ester with ethyl acetate by means of sodium were not successful.

O-*Benzylsyringic Acid and its Chloride* (XV) *and Amide*.—(A) Benzyl chloride (6·3 g.) was added to a solution of syringic acid (5 g.) in 10% aqueous sodium hydroxide (20 c.c.), and the mixture boiled until it became neutral; a further quantity (10 c.c.) of 10% sodium hydroxide was then added drop-wise. The isolated acids were separated by taking advantage of the more sparing solubility of the benzylated derivative in hot water; 4—4·5 g. of benzylsyringic acid, m. p. 140—150°, were obtained. It is better to prepare the acid by the hydrolysis of its methyl ester (above).

(B) The solution obtained by heating a mixture of methyl O-benzylsyringate (96 g.) and 10% aqueous sodium hydroxide (140 c.c.) for 2 hours on the steam-bath was cooled, diluted to 500 c.c., and acidified. The crude *acid* was crystallised from 95% alcohol (yield, 87 g.; m. p. 155—157°) and then from water or more dilute aqueous alcohol, forming slender, colourless prisms, m. p. 157° (Found: C, 66·7; H, 5·6. $C_{16}H_{16}O_5$ requires C, 66·6; H, 5·6%). A solution of the acid in sulphuric acid is bright yellow and soon becomes bluish-green.

Graebe and Martz (*Ber.*, 1903, **36**, 217) describe the formation of syringic acid from gallic acid trimethyl ether by the action of concentrated hydrochloric acid at 150°. Debenzylation of O-benzylsyringic acid is much more facile, occurring to a large extent in 3 or 4 minutes under the influence of boiling 20% hydrochloric acid.

Owing to this ease of debenzylation some difficulty was experienced in finding the conditions for the preparation of O-*benzylsyringoyl chloride*. Powdered phosphorus pentachloride (41·6 g.) was added during 30—40 minutes to a suspension of powdered O-benzyl-

syringic acid (57·6 g.) in benzene (200 c.c.) efficiently cooled by ice. The mixture was occasionally shaken during 4—5 hours and the solid had then passed into solution. Crushed ice was added to decompose the phosphoryl chloride and in sufficient amount to keep the mixture near 0°. The separated henzene layer was washed with ice-water, aqueous potassium bicarbonate, and ice-water and dried with calcium chloride, and the solvent was removed, finally under diminished pressure. The residual pale yellow oil crystallised to a nearly colourless mass (46 g.), m. p. 35—40°, sufficiently pure for many purposes.

The chloride is readily soluble in most organic solvents and separates from light petroleum in colourless needles, m. p. 45° (Found: C, 62·9; H, 5·0. $C_{16}H_{15}O_4Cl$ requires C, 62·6; H, 4·9%).

When an emulsion of the chloride (1 g.) and water was shaken with 15% aqueous ammonia (10 c.c.), the *amide* was at once precipitated. It crystallised from alcohol in colourless, elongated plates, m. p. 152° (Found: C, 66·4; H, 5·9. $C_{16}H_{17}O_4N$ requires C, 66·9; H, 6·0%).

Ethyl O-*Benzylsyringoylacetoacetate and Ethyl* O-*Benzylsyringoylacetate* (XIV).—Sodium (9·2 g.) was dissolved in alcohol, and the solution made up to 150 c.c. Half of the ethoxide was added to a mixture of ethyl acetoacetate (26 g.) and ether (50 c.c.) well cooled in ice. *O*-Benzylsyringoyl chloride (30·6 g.) in ether (50 c.c.) was then gradually introduced with shaking and continued cooling. After 1 hour the alternate addition of the sodium ethoxide solution (38 c.c., 19 c.c., 9·5 c.c., remainder) and of benzylsyringoyl chloride (15·3 g., 7·7 g., 3·8 g., 3·8 g.) in ether was commenced under conditions similar to those previously observed. After 12 hours, the mixed sodium salts were collected, washed with ether, and added to ice-cold, dilute hydrochloric acid in the presence of ether. The ethereal solution was dried and the solvent removed, leaving a residue which solidified to an almost colourless mass (67 g.). After one crystallisation from methyl alcohol the m. p. was 74—84° and after three further crystallisations fine, colourless needles, m. p. 97—102°, were obtained (Found: C, 65·9; H, 5·7. $C_{22}H_{24}O_7$ requires C, 66·0; H, 6·0%). The *ester* is readily soluble in benzene, chloroform and methyl alcohol and separates very slowly from its saturated solution in the last solvent; it is sparingly soluble in boiling light petroleum. An alcoholic solution develops a crimson coloration with ferric chloride, and the orange solution in sulphuric acid soon becomes crimson. The ester is soluble in aqueous sodium carbonate and is precipitated unchanged on acidification.

Finely powdered ethyl *O*-benzylsyringoylacetoacetate (50 g.) was added to water (2000 c.c.), ammonium chloride (80 g.), and con-

centrated aqueous ammonia (200 c.c.). The solution became opalescent and deposited an oil; after 2 hours the original ester had passed into solution and the hydrolysed product had separated completely from the clear liquid. The ester was crystallised from methyl alcohol (yield, 32 g.; m. p. 64—66°) and finally obtained in prisms, m. p. 67° (Found: C, 67·2; H, 6·0. $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·2%).

Ethyl O-*benzylsyringoylacetate* is readily soluble in methyl alcohol and very readily soluble in benzene or chloroform; it is sparingly soluble in light petroleum and separates from this solvent in iridescent plates. A crimson coloration is developed with alcoholic ferric chloride.

Copper derivative. Under the usual conditions, many derivatives of ethyl benzoylacetate are difficult to transform into their copper salts, but we have found (compare J., 1926, 2364) that the derivatives are readily obtained by the interaction of the esters and copper acetate in pyridine solution. The *copper* derivative of ethyl benzylsyringoylacetate prepared in this way and precipitated on the addition of water, crystallised from benzene in pale green needles, m. p. 212° (Found: Cu, 8·3. $C_{40}H_{42}O_{12}Cu$ requires Cu, 8·2%).

ω-*Benzoyloxy-4-benzyloxy-3 : 5-dimethoxyacetophenone* (XVI).—Ethyl O-benzylsyringoylacetate (7·2 g.) was converted into its potassium salt by means of pulverised potassium (0·78 g.) in benzene suspension. The mixture was then cooled in ice during the addition of benzoyl peroxide (4·85 g.), dissolved in a little benzene. The reaction evidently proceeded smoothly, since the aqueous washings were neutral, and the product was a viscous, pale yellow oil, which gave only a very weak ferric chloride reaction and reduced Fehling's solution very readily on warming. It could not be crystallised and was therefore directly hydrolysed by heating with an equal volume of water in a sealed tube at 160—170° for 8 hours. The resulting oil was dissolved in benzene and washed with dilute aqueous sodium hydroxide. This dissolved about 30—40% of the material, and the acid obtained on acidification was, rather unexpectedly, benzylsyringic acid; no syringic acid could be isolated and only a small quantity of benzoic acid was present. The benzene solution was washed with water and dried, and the solvent removed, leaving an oil that partly crystallised and was allowed to remain in contact with porous porcelain. The substance crystallised from methyl alcohol in slender, colourless prisms, m. p. 105° (Found: C, 70·6; H, 5·5. $C_{24}H_{22}O_6$ requires C, 70·9; H, 5·5%). The *ketone* is readily soluble in benzene, sparingly soluble in the simple alcohols, and very sparingly soluble in light petroleum. It appeared to condense with O-benzoylphloroglucinaldehyde, although in a

sluggish fashion, and the behaviour of the substance in this and other respects was somewhat anomalous.

In one experiment, the aqueous solution from the hydrolysis of the crude benzoyloxylated product deposited a crystalline substance m. p. 87—89°, which reduced Fehling's solution in the cold and condensed readily with *O*-benzoylphloroglucinaldehyde to a flavylium salt. This substance was doubtless ω-hydroxy-4-benzyloxy-3 : 5-dimethoxyacetophenone (XVII), but the conditions for its preparation could not be ascertained. The flavylium salt (from 0·08 g. of the carbinol) was debenzoylated in the usual manner and furnished a salt agreeing with malvidin in regard to the colour of acid solutions, the behaviour with ferric chloride, and the alkali-colour-reaction.

Experiments on the action of acetyl peroxide in ethereal solution on the potassio-derivative of ethyl benzylsyringoylacetate were undertaken. An excess of barium peroxide was employed in the preparation of the ethereal solution, the concentration of which (9·65 g. contained 1 g. of the peroxide) was estimated by combined iodometric and acidimetric methods; acetic anhydride was not present in significant proportion. Ethyl benzylsyringoylacetate (14·9 g.) was converted into its potassio-derivative under benzene and oxidised below 15° by means of the ethereal acetyl peroxide (55 c.c.). The reaction proceeded normally, but the isolated product gave a ferric chloride reaction and therefore contained unchanged ester. This was removed in the form of its copper derivative by the pyridine–copper acetate method. The separated oil then gave no immediate ferric chloride reaction and rapidly reduced Fehling's solution on warming. A crude benzoylcarbinol derivative was obtained from this product by means of boiling 5% sulphuric acid (10 hours), together with a small quantity of a similar substance, m. p. 85—87°, that crystallised in colourless prisms from the aqueous solution. The main, more sparingly soluble, product could not be crystallised, but it condensed readily with *O*-benzoylphloroglucinaldehyde in ethyl acetate solution in presence of hydrogen chloride, the dark red flavylium salt produced forming stout parallelopipeds having a marked yellowish-green lustre. This was debenzoylated and debenzylated, but although the salts at the various stages crystallised well, the reactions were not those of pure malvidin derivatives and indicated contamination with salts not containing a free hydroxyl group in position 3.

Ethyl Di(O-benzylsyringoyl)succinate. (XVIII).—(A) Powdered lead tetra-acetate (11·1 g.) (Dimroth and Schweitzer, *Ber.*, 1923, **56**, 1375) was added in several small portions to a solution of ethyl benzylsyringoylacetate (9·0 g.) in acetic acid (20 c.c., previously

crystallised and drained) with cooling in ice. After 12 hours, water was added, the product taken up in benzene and freed from acids by means of aqueous sodium carbonate, and the solution dried. The oily residue after removal of the solvent contained unchanged ester, because it gave a ferric chloride reaction, and it probably contained the α-acetoxy-derivative, because it reduced Fehling's solution; the substances responsible for these reactions were not isolated. The oil partly crystallised on keeping and, after draining on porous porcelain, the solid was recrystallised from methyl alcohol, forming flat, colourless prisms, m. p. 173—176° after softening at 168° (Found: C, 67·1, 67·3; H, 5·1, 5·5. $C_{40}H_{40}O_{12}$ requires C, 67·4; H, 5·7%). This ester is moderately readily soluble in benzene and chloroform and is sparingly soluble in methyl alcohol; it neither exhibits a ferric chloride reaction nor reduces Fehling's solution even on heating.

Conceivably the substance is $C_{40}H_{38}O_{12}$ (C, 67·6; H, 5·4%), that is, ethyl di(benzylsyringoyl)fumarate (or maleate), and this hypothesis is certainly favoured by the absence of a ferric chloride reaction. Subsequently we found that the action of lead tetraacetate on the potassium derivative of the ester in benzene suspension afforded the succinate (or fumarate) in improved yield.

(B) Potassium (0·39 g.) was pulverised under benzene, and ethyl benzylsyringoylacetate (3·6 g.) introduced. When the formation of the metallic derivative was complete a benzene solution of iodine (1·3 g.) was added with cooling. The reaction was completed by heating on the steam-bath for 30 minutes. The product crystallised from much methyl alcohol in flat, colourless prisms, m. p. 173—176°, unchanged by admixture with the specimen prepared by method (A).

The fused ester has a yellow colour and its solution in sulphuric acid is red. All its properties are in good agreement with the "fumarate" hypothesis, but the above method of preparation harmonises better with the view that the ester is a derivative of succinic acid.

ω-*Diazo-4-benzyloxy-3 : 5-dimethoxyacetophenone* (XIX).—A solution of benzylsyringoyl chloride (14·3 g.) in anhydrous ether was added during 5 minutes to an ethereal solution of diazomethane (from 20 c.c. of nitrosomethylurethane; compare Houben–Weyl, "Die Methoden der Organischen Chemie," 1923, 3, 124) previously distilled through an efficient column (45 cm.) and cooled to −10°. A mild evolution of nitrogen occurred and continued for 1—1½ hours and crystallisation of the product commenced 10 minutes after the reagents were mixed. Next day the pale yellow solid was collected (13·4 g., m. p. 116—120° with decomp.) and a further quantity (1·25 g., m. p. 105—108°, recryst., m. p. 118—120°) was obtained

from the ethereal solution. The new substance crystallised with great ease from a variety of solvents; it separated from benzene–light petroleum in bright lemon-yellow, quadrilateral tablets or flat prisms, m. p. 122—123° (decomp.) (Found: C, 64·7, 65·4, 65·5; H, 5·2, 4·8, 4·8; N, 8·8. $C_{17}H_{16}O_4N_2$ requires C, 65·4; H, 5·2; N, 9·0%).

This *diazo-ketone* is readily soluble in alcohol and benzene, sparingly soluble in ether, and very sparingly soluble in light petroleum. It was unchanged by boiling aqueous alcohol in a few minutes, but was rapidly decomposed by acids and by iodine in alcoholic solution with evolution of nitrogen. It gave no coloration with cold alcoholic sodium hydroxide, but on warming a crimson solution was obtained; ω-diazoacetophenone exhibits this reaction in the cold (Wolff, *Annalen*, 1902, **325**, 141). The thermal decomposition of the substance occurs vigorously at 125° or at lower temperatures with impure specimens. In *iso*amyl ether the diazo-ketone appeared to be stable at 130°, but on the addition of porous porcelain, nitrogen was evolved and a sparingly soluble oil separated. The product of decomposition in a vacuum crystallised from light petroleum in bundles of colourless, flat prisms, m. p. 58—59°.

The action of boiling dilute aqueous-alcoholic sulphuric acid on the diazo-ketone gave a compound that crystallised from light petroleum, containing a little benzene, in colourless needles, m. p. 85—86°. The substance was soluble in hot water and crystallised on cooling; it rapidly reduced Fehling's solution in the cold and was undoubtedly *O-benzylsyringoylcarbinol* (XVII). The *diphenylhydrazone* of the related phenylglyoxal derivative crystallised from aqueous pyridine in bright yellow, slender prisms, m. p. 131° after sintering at 110°.

*ω-Acetoxy-4-benzyloxy-*3 : 5-*dimethoxyacetophenone* (XX).—A mixture of the crude diazo-ketone (15 g., m. p. 115—120°) and acetic acid (30 c.c.) was heated at 60—70° until the evolution of nitrogen ceased and was then boiled for 2 minutes. Ether was added to the cooled liquid, and the acetic acid removed by washing with aqueous sodium carbonate; the washed and dried ethereal solution was then evaporated, and the residue extracted by means of boiling light petroleum. The first extracts readily deposited colourless crystals (5·7 g.), m. p. 58—60°, but the later extracts were contaminated with a yellow oil and crystallised much more slowly; on keeping, however, crystals were obtained from these fractions also and had the m. p. 57—60° (8·0 g.). About 2 g. of a deep yellow material remained undissolved. The *ketone* crystallised from light petroleum in colourless, fibrous, prismatic needles, m. p. 60·5—61° (Found: C, 66·1; H, 5·7. $C_{19}H_{20}O_6$ requires C, 66·2; H, 5·9%).

It is freely soluble in alcohol, benzene, or chloroform and it is rapidly oxidised by warm Fehling's solution.

5-Benzoylmalvidin Chloride (XXI).—Hydrogen chloride was passed into a filtered solution of ω-acetoxy-4-benzyloxy-3 : 5-dimethoxyacetophenone (2·2 g., m. p. 58—60°) and pure *O*-benzoylphloroglucinaldehyde (2·1 g., m. p. 196°) in ethyl acetate (40 c.c., distilled over phosphoric oxide) cooled to 0°. A colourless solid separated slowly during 1—1½ hours, but this did not increase in amount and after 7 hours it was collected. The filtrate was kept saturated with hydrogen chloride and next day a dark red crystalline powder had separated (1·2—1·3 g. Specimen A). A further quantity (0·61 g.) of less pure material separated on keeping for 48 hours. The salt crystallised from methyl alcohol–10% hydrochloric acid in well-formed, oblique, elongated prisms which were olive-green in mass and exhibited a strong golden lustre (Found in air-dried material: C, 56·1, 56·0; H, 4·1, 4·0. $C_{24}H_{19}O_8Cl,2{\cdot}5H_2O$ requires C, 55·9; H, 4·6%). Benzoylmalvidin chloride is moderately readily soluble in methyl alcohol, more sparingly so in ethyl alcohol, to violet-red solutions which are readily decolorised on keeping or heating. The salt dissolves in hot water to a colourless solution containing the pseudo-base and even the solution in 0·5% hydrochloric acid is decolorised on boiling for a few minutes. The solution in hot 4% hydrochloric acid is stable and has a weak bluish-red colour. Aqueous sodium carbonate dissolves the salt to a pure deep blue solution, which becomes greener on dilution with water, and in alcoholic solution even the addition of sodium acetate gives a pure blue coloration. The ferric chloride reaction is negative and the violet-red solution in concentrated sulphuric acid does not exhibit fluorescence.

In a second experiment the acetoxy-ketone (3·45 g.) and *O*-benzoylphloroglucinaldehyde (3·25 g.) were condensed together in ethyl acetate (100 c.c.); after the solution had been saturated at 0°, the temperature was allowed to rise to that of the room. The colourless product (0·95 g.) that separated was collected after 5 hours and consisted of benzoylphloroglucinaldehyde. The filtrate was maintained saturated for 12 hours and the benzoylmalvidin chloride separated in dark red, flat, quadrilateral prisms, which appeared olive-green in mass and had a striking golden-yellow lustre (yield, 1·55 g.). Further quantities were obtained on keeping (24 hours, 0·8 g.; 48 hours, 0·1 g.; 96 hours, 0·15 g.) and the total yield was 2·6 g. (Specimen B).

Malvidin Chloride (II).—Benzoylmalvidin chloride (1·0 g. of A) was dissolved in 10% aqueous sodium hydroxide (10 c.c.) and a stream of hydrogen was used to exclude air and to agitate the

mixture. The colour changed from deep blue to green and finally to orange. After 4½ hours methyl alcohol (20 c.c.) and concentrated hydrochloric acid (4 c.c.) were added, giving a clear violet-red solution, which was heated on the steam-bath for ½ hour and kept over-night. A quantity (about 0·5 g.) of malvidin chloride crystallised in stout prisms possessing a marked steel-blue lustre when in contact with the solvent and appearing olive-green in mass (Specimen C). About 0·2 g. of less pure material was obtained from the mother-liquor on the addition of 10% hydrochloric acid.

A second specimen of the salt was prepared from benzoylmalvidin chloride (2·55 g. of B) by hydrolysis with 10% aqueous sodium hydroxide (20 c.c.) for 5 hours. Regeneration of the pyrylium salt was effected by means of concentrated hydrochloric acid (6·5 c.c.) and ethyl alcohol (20 c.c.); a portion of the malvidin chloride crystallised during the ½ hour period of heating on the steam-bath. The appearance of the product resembled that of C; it was collected after 12 hours and washed with aqueous-alcoholic hydrochloric acid and ether (yield, 0·9 g.). The substance was recrystallised by solution in a boiling mixture of ethyl alcohol (4 vols.; more than 400 c.c. were required) and 10% hydrochloric acid (1 vol.) and addition of hot 10% hydrochloric acid (3 vols.) to the filtered solution. The malvidin chloride (Specimen D) was deposited in small, flat, rhombic prisms or tablets which appeared red by transmitted light and had a green lustre in mass when dry or a steel-blue lustre when in contact with the solvent (Found in air-dried material: C, 53·0, 53·4; H, 3·7, 4·1; MeO, 15·8; loss at 110° in a high vacuum, 4·1. Calc. for $C_{17}H_{15}O_7Cl,H_2O$: C, 53·0; H, 3·9; 2MeO, 16·1; H_2O, 4·7%). The anhydrous salt was extremely hygroscopic and absorbed water from the air during weighing; hence the somewhat low value found for loss at 110° in a high vacuum. Every statement made by Willstätter and Mieg (*loc. cit.*) from "*Bei 300° ist die Substanz*" (p. 132) to "*rotbraunen Nädelchen aus.*" (end of p. 133) in regard to the properties of malvidin chloride was confirmed with the synthetical specimens in detail (the solubility in 7% sulphuric acid was not, however, quantitatively determined). In addition, Specimen C was directly compared with malvidin chloride obtained by the hydrolysis of the malvin chloride so kindly sent to us by Professor Karrer. This material had a chocolate-brown colour and exhibited a strong tendency to crystallise in slender needles. It dissolved in methyl alcohol and immediately crystallised again, as described by Willstätter and Mieg. This product was easily soluble in 0·01% hydrochloric acid and when warmed with 0·5—1% hydrochloric acid it also dissolved, but crystallised from the hot solution in highly characteristic, very small, hair-like needles which were very spar-

ingly soluble in cold 0·01% hydrochloric acid. This whole process had to be repeated twice in order to obtain a completely homogeneous crystallisation from the dilute hydrochloric acid. (C) behaved in the same way; it dissolved in methyl alcohol, and a blood-red crystalline powder, violet by transmitted light, soon separated. The material had the same bright reflex, resembling that of iron pyrites, as the natural specimen and, like it, consisted of obliquely cut, elongated prisms. On treatment with 0·5% hydrochloric acid it also dissolved and on heating crystallised again in needles, rather larger than those from the natural specimen. After several repetitions, the product was very sparingly soluble in cold 0·01% hydrochloric acid and its solubility in 0·5% hydrochloric acid at 55° was found (colorimetric comparison) to be within 5% of that of the specimen of natural origin. The synthetical specimen was a shade the more sparingly soluble of the two.

The solubility of malvidin chloride in cold, very dilute hydrochloric acid is entirely a question of crystalline form. Most specimens dissolve very easily in 0·01% hydrochloric acid and even in 0·1% acid to brownish-red solutions, which are possibly hydrolysed and possibly colloidal; the test with 0·01% hydrochloric acid is an extraordinarily stringent one and will succeed only with material which has been prepared as described above and found to be microscopically homogeneous. If any indefinitely crystallised aggregates are present, the 0·01% hydrochloric acid will dissolve them. The colour of alcoholic solutions at various stages of dilution and on the addition of hydrochloric acid, sodium acetate, and sodium carbonate, the rates of pseudo-base formation and oxidation by hydrogen peroxide, and the extent of recovery of the salt from the pseudo-base were directly quantitatively compared and found to be completely identical in the case of the natural and the synthetic specimen.

The only remaining point to be cleared up was the difficulty that we had never observed, nor had other authors described, the crystallisation of malvidin chloride in rhombic plates as recorded above. We attributed this to the exceptional purity of the synthesised salt and accordingly attempted the purification of the anthocyanidin. After separation from methyl alcohol, the picrate was prepared and crystallised from a methyl-alcoholic solution of picric acid. The recovered chloride was again crystallised from methyl alcohol and afterwards from a mixture of ethyl alcohol and 10% hydrochloric acid under the conditions mentioned above. At first, prismatic needles separated; a second crystallisation gave clusters of rather indefinite prisms, and a third crystallisation with slow cooling gave rhombic prisms, not quite so clear-cut as those of the Specimen D but obviously of the same crystalline habit. It was very interesting

to note the appearance of the steel-blue lustre of the crystals in suspension in the solvent and the green reflex of the dried salt. The solubility of (D) in hot aqueous alcoholic hydrochloric acid was greatly increased on the addition of a trace of peonidin chloride. The salt separated in indefinite clusters of jagged prisms and the mother-liquor deposited, on evaporation in the air, very slender needles exactly like those of natural malvidin chloride. We do not suggest that the impurity in natural malvidin is necessarily peonidin (although malvidin may contaminate peonidin), but undoubtedly malvidin chloride from natural sources does contain some persistent impurity that modifies its habit of crystallisation. This impurity does not give a ferric chloride reaction, and this fact points to peonidin. Both peonidin chloride and malvidin chloride have been obtained synthetically in a well-defined prismatic form exhibiting a characteristic lustre; on the other hand, the anthocyanidins from natural sources are usually chocolate-brown and devoid of marked lustre. Mixtures of the synthetic malvidin with a little synthetic peonidin or of the synthetic peonidin with a little synthetic malvidin also tend to crystallise in forms which when dried are almost lustreless and chocolate-brown.

4-Benzyloxy-3 : 5-dimethoxyacetophenone (XXII) *and 4-Hydroxy-3 : 5-dimethoxyacetophenone*.—The hydrolysis of ethyl *O*-benzylsyringoylacetate by means of 5% or 10% aqueous sulphuric acid did not proceed satisfactorily, but the acetophenone derivative could be readily obtained under the following conditions. Ethyl benzylsyringoylacetate (12 g.) was heated with water (10 c.c.) in a sealed tube at 175—180° for 10 hours. The product was taken up in benzene, the extract washed with aqueous sodium hydroxide and water and dried, and the solvent removed, leaving a crystalline mass (9 g., m. p. 50—59°). The ketone crystallised from light petroleum in colourless, slender prisms, m. p. 60—61° (Found : C, 71·3; H, 6·3. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%); it is readily soluble in other organic solvents. The orange solution in sulphuric acid slowly became greenish-brown on keeping. The *semicarbazone* crystallised from aqueous alcohol in platelets, m. p. 166°. The 2 : 4-*dinitrophenylhydrazone* was prepared in dilute alcoholic solution and crystallised from benzene–alcohol in scarlet, prismatic needles, m. p. 192—193°.

The ketone (5·3 g.) was debenzylated during 7 hours by means of a cold saturated solution of hydrogen bromide in acetic acid (18 c.c.). *4-Hydroxy-3 : 5-dimethoxyacetophenone* crystallised from light petroleum in colourless, slender prisms, m. p. 117° (yield, 1·9 g.) (Found : C, 61·1; H, 6·2. $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·2%). The substance was soluble in aqueous sodium carbonate solution and

gave a precipitate of a sparingly soluble sodium salt when triturated with 15% aqueous sodium hydroxide. Its solution in sulphuric acid was yellow, and ferric chloride added to an alcoholic solution developed a weak bluish-green coloration. On treatment with benzyl chloride and potassium hydroxide in boiling aqueous methyl-alcoholic solution, the original ketone, m. p. 60—61°, was *regenerated. Attempts to obtain this substance directly from the* accessible pyrogallol 1 : 3-dimethyl ether were unsuccessfully made by Mr. L. R. Ridgway. The phenol did not react with acetonitrile under the conditions of the Hoesch synthesis. A solution of the phenol (6 g.) and acetyl chloride in carbon disulphide was treated with anhydrous ferric chloride and kept in the cold for 16 hours. 2·1 G. *of a substance, crystallising from benzene–light* petroleum in shining leaflets, m. p. 110° (phenylhydrazone, m. p. 106—107°), and insoluble in aqueous sodium carbonate, were obtained. These data show that the product of this reaction was 3-acetoxy-2 : 4-dimethoxyacetophenone (compare Brand and Collischonn, *J. pr. Chem.*, 1922, **103**, 338). Even if the hydroxyl group were not first acetylated, it is doubtful whether the acetyl group would enter the desired position para to hydroxyl, since Levine (*J. Amer. Chem. Soc.*, 1926, **48**, 797, 2719) has shown that the bromination and chlorination of pyrogallol 1 : 3-dimethyl ether occur in position 4. The reaction was carried out in a neutral solvent and the result may be attributed to the absence of *active* anions and the consequent relative immunity of the proton of the hydroxyl group. In such circumstances, the directive power of hydroxyl relative to that of methoxyl is greatly diminished. Chlorination of benzyloxydimethoxyacetophenone occurred readily, but the halogen atom appeared to enter the nucleus preferentially. The most advantageous method of preparation of iso*nitroso-4-benzyloxy-3 : 5-dimethoxyacetophenone*,

$$CH_2Ph{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CH{:}NOH,$$

was found to be the following: Ethyl alcohol (4 g.) was added to a suspension of pulverised sodium (1·2 g.) in dry ether (70 c.c.), and when the formation of the ethoxide was complete the mixture was cooled in ice and benzyloxydimethoxyacetophenone (10 g.) and freshly distilled *iso*amyl nitrite (6·1 g.) were successively introduced, the latter in small portions during 1 hour. The amount of the yellow sodium salt that separated increased during several days and after 5 days the solid was collected, washed with ether, and dissolved in water. The crude *isonitroso*-derivative was obtained by acidification with acetic acid and freed from 1·5 g. of benzylsyringic acid by washing its solution in benzene with aqueous sodium carbonate. The derivative (yield, 6·0 g.) crystallised from light petroleum, containing a little chloroform, in canary-yellow, flat

prisms, m. p. 107—108° (Found: N, 4·8. $C_{17}H_{17}O_5N$ requires N, 4·5%). The substance has the usual properties of its class and forms an *oxime* that crystallises from aqueous alcohol in colourless, slender, flat prisms, m. p. 141—142°. A dilute solution of this dioxime in 50% aqueous ethyl alcohol gave orange-red and reddish-brown precipitates on the addition of aqueous nickel and cobalt acetates, respectively.

5 : 7 : 4'-*Trihydroxy*-3' : 5'-*dimethoxyflavylium Chloride* (XXIII).—A stream of dry hydrogen chloride was passed through an ice-cold solution of 4-benzyloxy-3 : 5-dimethoxyacetophenone (3·0 g.) and *O*-benzoylphloroglucinaldehyde (4·0 g.) in dry ethyl acetate (70 c.c.) for 10 hours. The reddish-bronze crystals were then isolated (4·3 g.); they possessed a marked greenish-yellow lustre. This substance, which was very probably a mixture, was debenzoylated by means of 10% aqueous sodium hydroxide (passage of hydrogen) in 6 hours. The reddish-orange alkaline liquid was then mixed with methyl alcohol and concentrated hydrochloric acid, and the flavylium salt regenerated by heating on the steam-bath for ½ hour. The crude salt was crystallised from methyl alcohol containing hydrogen chloride and then from alcohol and a few drops of concentrated hydrochloric acid. This material was next fully debenzylated, whereby the facility with which the substance crystallised was greatly increased; the crystalline habit was modified, but there was no great change in the colour reactions. The salt (0·47 g.) was dissolved in acetic acid (50 c.c.), and hydrogen chloride passed in, first at 15°, and then at 65—70° for 2 hours. Crystals remained in suspension and these together with a crop obtained on cooling were recrystallised, first from ethyl alcohol and a few drops of hydrochloric acid and then from methyl alcohol containing a little hydrochloric acid. The homogeneous product consisted of slender, pointed, hexagonal prisms, reddish-brown in colour and exhibiting a greenish-yellow lustre when rubbed, m. p. 280° (Found: C, 55·2, 55·3; H, 4·4, 4·5; Cl, 9·3. $C_{17}H_{15}O_6Cl,H_2O$ requires C, 55·4; H, 4·6; Cl, 9·6%).

5 : 7 : 4'-*Trihydroxy*-3' : 5'-*dimethoxyflavylium chloride* is very sparingly soluble in cold water to a yellow solution, but readily soluble in hot water to a deep brownish-red solution (basic salt); it is very sparingly soluble in hot dilute hydrochloric acid. The brownish-red solution in methyl alcohol has a faint violet nuance and the colour is not discharged by dilution or by heating. In this respect, the salt exemplifies the rule that pseudo-base formation of a hydroxyflavylium salt that can give a colour-base is associated with the occurrence of the groups OH or OR in position 3. The dichroic solution in aqueous sodium carbonate is reddish-violet and

the colour remains unchanged on the addition of alcohol. The colour in aqueous sodium hydroxide is also reddish-violet, but changes through deep red to orange and yellow. Sodium acetate added to a methyl-alcoholic solution develops a reddish-violet coloration and the solution appears bluish-purple in thin layers.

4-Hydroxy-ω : 3 : 5-trimethoxyacetophenone (XXIV).—Ethyl αγ-dimethoxyacetoacetate (12·0 g.) (Pratt and Robinson, J., 1925, **127**, 168) was added to a suspension of sodium powder (1·45 g.) in anhydrous ether (100 c.c.), and when the formation of the sodio-derivative was complete powdered acetylsyringoyl chloride (15·5 g.) was added in one portion. Next day the mixture was refluxed for 4 hours. The product crystallised in sheaves of colourless plates and gave a deep red coloration with alcoholic ferric chloride.

This intermediate was mixed with water (100 c.c.), and a solution of potassium hydroxide (16·5 g.) in water (25 c.c.) introduced at intervals during 2 days. The deep orange solution was then boiled for 4 hours; on cooling, a sparingly soluble yellow potassium salt separated and more of this was obtained by the addition of potassium hydroxide (20 g.) in water (15 c.c.) to the filtrate. The derivative was collected on a sintered glass filter, washed with 20% potassium hydroxide, and added to an excess of dilute hydrochloric acid. The ketone quickly solidified (yield, 1·4 g.) and then crystallised from light petroleum in colourless, elongated prisms, m. p. 90° (Found: C, 58·4; H, 6·0. $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%). *4-Hydroxy-ω : 3 : 5-trimethoxyacetophenone* is readily soluble in most organic solvents, and forms yellow solutions in dilute aqueous alkalis. A weak green coloration (similar to that given by ω-chloroacetovanillone) is produced by alcoholic ferric chloride.

5 : 7 : 4′-Trihydroxy-3 : 3′ : 5′-trimethoxyflavylium Chloride (*Malvidin Chloride 3-Methyl Ether*) (XXV).—*5-Benzoyl derivative*. An ice-cold solution of 4-hydroxy-ω : 3 : 5-trimethoxyacetophenone (1·05 g.) and *O*-benzoylphloroglucinaldehyde (2·0 g.) in dry ethyl acetate (35 c.c.) was saturated with hydrogen chloride for 10 hours. Next day the dark violet oxonium salt was collected (2·1 g.); it crystallised from methyl alcohol, containing a little 8% hydrochloric acid, in glistening rhombs, deep red by transmitted light, olive-green by reflected light, and possessing a bright yellow lustre (Found: C, 57·6, 57·4. $C_{25}H_{21}O_8Cl,2H_2O$ requires C, 57·7%).

The salt dissolved readily in hot water to a red solution that rapidly became colourless; the colour was quickly and completely restored on the addition of hydrochloric acid. In cold 0·5% hydrochloric acid a pale red solution was obtained, but hot 8% hydrochloric acid was only coloured pink. The red solution in methyl alcohol had a violet tinge and was decolorised on dilution with more

methyl alcohol. The powdered salt was coloured blue by moderately concentrated aqueous sodium carbonate, but not dissolved; on the addition of methyl alcohol a blue solution resulted and this was greener than the corresponding solution of the de-benzoylated salt (below). Similarly the violet colour obtained by the addition of solid sodium acetate to a solution of the salt in methyl alcohol was slightly bluer than that given by the malvidin 3-methyl ether under the same conditions.

De-benzoylation. A stream of hydrogen was passed through ice-cold 10% aqueous sodium hydroxide (20 c.c.), and the crude benzoyl derivative (2·0 g.) stirred into the solution. The purplish-blue colour persisted for 45—50 minutes and subsequently changed through olive-green to deep orange. After 6 hours, methyl alcohol (20 c.c.) and concentrated hydrochloric acid (6 c.c.) were added, the clear red solution was heated to incipient ebullition for 30 minutes and kept for 12 hours, and the flavylium salt was then precipitated by means of concentrated hydrochloric acid. It was collected and twice separated as an amorphous violet-brown powder from hot 3% hydrochloric acid. Crystallisation from methyl alcohol under a variety of conditions was unsuccessfully attempted, but the salt crystallised easily from ethyl alcohol, containing a few drops of concentrated hydrochloric acid, as a dark violet powder having a bright yellow reflex and consisting of slender prisms that appeared deep red by transmitted light (Found in air-dried material: C, 55·7, 55·7; H, 5·2, 5·4. $C_{18}H_{17}O_7Cl,\frac{1}{2}H_2O$ requires C, 55·5; H, 4·9%). This malvidin chloride methyl ether is much more readily soluble in water and dilute hydrochloric acid than its benzoyl derivative or malvidin chloride; in cold water the solution has a blood-red colour and is decolorised on keeping, if sufficiently dilute. The cold saturated solution in 3% hydrochloric acid is deep red and even in hot 8% hydrochloric acid the salt is moderately readily soluble, but separates almost completely on cooling. It is readily soluble in methyl alcohol, but sparingly so in ethyl alcohol, and the colour of the acid alcoholic solutions resembles that of malvidin. The ease of pseudo-base formation in alcoholic solution is greater than with malvidin and the colour is immediately and fully restored on acidification. An alcoholic solution added to much water gives a solution of the damson colour-base, from which the pseudo-base is formed at a measurable rate. The solutions in aqueous sodium carbonate and aqueous sodium hydroxide are purplish-blue and change very little on the addition of alcohol; the colorations are redder than those characteristic of malvin or malvidin under the same conditions.

The colorations produced by the addition of sodium acetate to

solutions of the salt are violet, and bluer in methyl alcohol than in water. Addition of aqueous sodium acetate to a concentrated *methyl-alcoholic solution precipitates* the violet colour-base, insoluble in water but immediately soluble in dilute hydrochloric acid to a red solution.

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THE UNIVERSITY, MANCHESTER. [*Received, May 3rd*, 1928.]

CCIV.—*The Constitution of Phenolphthalein. Part I. Preparation of Some Compounds of the Phthalein Type.*

By HAKON LUND.

THE constitutions of phenolphthalein and its coloured derivatives have been thoroughly discussed by many chemists and different theories have been put forward to explain the intense colour of the salts of phenolphthalein and similar compounds. Friedländer (*Ber.*, 1893, **26**, 173) was the first to suggest the usually accepted theory that one of the phenol groups is transformed into a quinonoid group when phenolphthalein reacts with one or two molecules of alkali :

$$\begin{matrix} HO{\cdot}C_6H_4{\cdot}C{\cdot}C_6H_4{\cdot}OH \\ C_6H_4{<}{\underset{CO}{}}{>}O \end{matrix} + 2\bar{O}H \longrightarrow \begin{matrix} O{:}C_6H_4{:}C{\cdot}C_6H_4{\cdot}\bar{O} \\ C_6H_4{<}CO{\cdot}\bar{O} \end{matrix} + 2H_2O.$$

The discussion has, however, not yet led to any conclusive result. The latest work * dealing with the constitution of phenolphthalein and related substances is that of Birge and Acree (*J. Amer. Chem. Soc.*, 1919, **41**, 1031, where reference is given to a series of preceding papers), who have presented a " quinone phenolate " theory for the coloured compounds in the phthalein series. In this paper, they promise an extensive investigation which, unfortunately, seems to have been interrupted. Some of the experiments there suggested will be dealt with in the present investigation, although from another point of view.

The purpose of this investigation is to examine a series of phthalein compounds in regard to their physico-chemical properties. It is hoped that it will be possible to bring the halochromism of these

* When this communication was submitted for publication the author had no knowledge of the papers by Thiel and his co-workers (*Sitzungsber. Ges. Beförd. gesamt. Naturwiss. Marburg*, 1927, **62**, 471). Their results will be discussed in a future paper.

compounds into close relationship with that of the common triphenylcarbinol derivatives, some of which were studied a few years ago (*Dissert.*, Copenhagen, 1926. See also *J. Amer. Chem. Soc.*, 1927, **49**, 1346). The theoretical treatment of the subject will, however, be given in a subsequent paper. Here only the preparation of a number of new phthaleins and some of their purely chemical properties will be described.

In order to examine the influence of the carboxyl group *4-carboxy-2′ : 4′ : 6′ : 2″ : 4″ : 6″-hexamethoxytriphenylcarbinyl acetate* (II) was prepared by condensing terephthalaldehydic acid (1 mol.) with phloroglucinol trimethyl ether (2 mols.) by means of hydrogen chloride and oxidising the product, 2′ : 4′ : 6′ : 2″ : 4″ : 6″-*hexamethoxytriphenylmethane-4-carboxylic acid* (I), in glacial acetic acid solution with lead tetra-acetate. The *perchlorate* also was prepared; the carbinol-acid itself and its anhydride were too unstable to be isolated.

(I.) $CO_2H \cdot C_6H_4 \cdot CH[C_6H_2(OMe)_3]_2$ $\qquad$ $CO_2H \cdot C_6H_4 \cdot C(OAc)[C_6H_2(OMe)_3]_2$ (II.)

In the attempt to prepare the corresponding *o*-phthalic derivative in a similar way, *2′ : 4′ : 6′-trimethoxyphenylphthalide* (III) was obtained, the condensation taking place between only one molecule each of phloroglucinol trimethyl ether and *o*-phthalaldehydic acid. *Phloroglucinolphthalein hexamethyl ether* (IV) had to be made from phthalyl chloride, anhydrous zinc chloride being used as a condensing agent; it is colourless in neutral solution, whereas (II) is strongly coloured even when it is neutralised with one molecule of sodium hydroxide.

(III.) $C_6H_4<{CH \cdot C_6H_2(OMe)_3 \atop CO}>O$ $\qquad$ $C_6H_4<{C[C_6H_2(OMe)_3]_2 \atop CO}>O$ (IV.)

Resorcinolphthalein tetramethyl ether, $C_6H_4<{C[C_6H_3(OMe)_2]_2 \atop CO}>O$ (V),

was prepared in order to compare it with phenolphthalein dimethyl ether and (IV) in regard to their behaviour towards bases and acids. Phenolphthalein dimethyl ether dissolved in alcoholic potassium hydroxide, forming the compound $C_6H_4(CO_2K) \cdot C(OH)(C_6H_4 \cdot OMe)_2$; this remained in solution when water was added, provided that excess of alkali was present. Compound (V) also dissolved, forming an analogous salt; but on dilution with water this salt slowly split off potassium hydroxide and (V) was precipitated quantitatively. Compound (IV) did not react at all with potassium hydroxide: 1 mol. was boiled for an hour with 30 mols. of potassium hydroxide in the minimum quantity of alcohol necessary for dissolving the

compound; on cooling, however, a portion of the original compound crystallised, and the remainder was immediately precipitated on dilution with water.

Towards acids the three compounds behave similarly to the *non-carboxylated, methoxy-substituted triphenylcarbinols: with* increasing number of methoxy-groups the tendency to form coloured salts with acids increases. For instance, phenolphthalein dimethyl ether is only slightly coloured in concentrated hydrochloric acid, whereas the hexamethoxy-compound (IV) is strongly coloured in 10% hydrochloric acid. The great difference in absolute "basicity" of similarly substituted compounds of the two classes will be discussed in a subsequent paper.

During the work with the polymethoxylated triphenylcarbinols, it was observed that compounds containing two phloroglucinol trimethyl ether groups were very unstable in the presence of acids. The same proved to be the case with the compound (IV). In order to check the constitution of this compound it was intended to reduce it to the corresponding phthalin. Usually the best reducing agent for the polymethoxylated triphenylcarbinols is a solution of hydrochloric acid in alcohol. The compound (IV) dissolved in this medium, forming a strongly coloured solution which gradually lost its colour exactly as was to be expected. But no odour of acetaldehyde could be detected, and the compound which crystallised was an acid with an equivalent weight of about 320 instead of 468. The reaction proved to be a splitting of the molecule:

$$(IV) + H_2O \longrightarrow CO_2H{\cdot}C_6H_4{\cdot}COR + RH,$$

where R denotes 2 : 4 : 6-trimethoxyphenyl.

When the compound (IV) was heated for a short time with a mixture of glacial acetic acid and concentrated hydrochloric acid, the reaction proceeded still farther:

$$(IV) + 2H_2O \longrightarrow C_6H_4(CO_2H)_2 + 2RH.$$

The phloroglucinol trimethyl ether could be recovered practically quantitatively, and the phthalic acid was identified through the fluorescein test.

Finally, unsymmetrical phthaleins of the type

$$C_6H_4{<}\begin{matrix}CR{\cdot}C_6H_4{\cdot}OH\\ \\ CO\end{matrix}{>}O \qquad (VI),$$

where R is 4-methoxyphenyl, 2 : 4-dimethoxyphenyl, or 2 : 4 : 6-trimethoxyphenyl, were prepared. 4′-Hydroxy-*o*-benzoylbenzoic acid was condensed with phenolic ethers by means of an agent which appears not to have been applied before, *viz.*, a solution of concentrated sulphuric acid in anhydrous ethyl ether. This mixture

has to only a small extent the splitting effect upon these compounds which makes hydrogen chloride, aluminium chloride, and stannic chloride unsuitable for this condensation.

Phenolphthalein monomethyl ether (VI; R = 4-methoxyphenyl) was described by Meyer and Spengler (*Ber.*, 1905, **38**, 1328) as being intensely red in alkaline solution. Later Green and King (*Ber.*, 1907, **40**, 3729) showed that this colour was due to the presence of some phenolphthalein. They drew the conclusion that an alkaline solution of the pure monomethyl ether would be colourless, since the red colour became weaker and weaker by repeated crystallisations. Actually, however, it is yellow, and the colour fades slowly, as does that of all the phenolphthaleins, in the presence of a large excess of alkali.

A fact which has hitherto been overlooked is that this compound only crystallises with solvent of crystallisation, *e.g.*, one half molecule of toluene. After the solvent has been removed by heating, the molten mass solidifies to a glass-like substance which can be kept for months without crystallising. When, however, it is covered with a solvent such as alcohol, benzene, or toluene, crystallisation sets in after a few minutes and the whole mass is soon transformed into loose crystals. The different melting points reported in the literature, therefore, are of very limited value, because the temperature at which the compound becomes liquid depends on the solvent used and on the rate of heating.

Phenolphthalein monomethyl ether is insoluble in sodium carbonate solution, but gives a yellow solution in dilute aqueous sodium hydroxide—a fact which furnishes a method of purification. *Resorcinolphenolphthalein* 2′ : 4′-*dimethyl ether* (VI) forms a yellow solution in sodium carbonate; and *phloroglucinolphenolphthalein* 2′ : 4′ : 6′-*trimethyl ether* is soluble with an intense yellowish-brown colour in secondary sodium phosphate solution, where the hydroxyl-ion concentration is much smaller. This shows that the phenolic hydrogen becomes more acidic with increasing substitution of methoxy-groups in the other benzene ring. This phenomenon will be more thoroughly discussed in a future paper.

Experimental.

2′ : 4′ : 6′ : 2″ : 4″ : 6″-*Hexamethoxytriphenylmethane-4-carboxylic Acid* (I).—Into a solution of phloroglucinol trimethyl ether (2 g.) and terephthalaldehydic acid (0·9 g.) in absolute alcohol (35 c.c.) hydrogen chloride was passed until crystallisation began. After an hour the crystals were collected (2·25 g.; yield, 80%) and recrystallised from alcohol and from toluene; m. p. 258—260° (corr.) (Found: C, 66·4; H, 5·9; equiv., by titration, 470. $C_{26}H_{28}O_8$ requires C, 66·6;

H, 6·0%; equiv., 468). This colourless compound is soluble in acetone and acetic acid and slightly soluble in alcohol.

4-Carboxy-2′ : 4′ : 6′ : 2″ : 4″ : 6″-hexamethoxytriphenylcarbinyl Acetate (II).—The preceding compound (1 g.) and lead tetra-acetate (1 g.) were left in glacial acetic acid at 50° for 4 hours and at room temperature over-night. 4·63 C.c. of *N*-sulphuric acid in glacial acetic acid were then added and the filtered solution was evaporated under reduced pressure at about 45°. The residue was twice dissolved in chloroform and precipitated with anhydrous ether, *yielding 0·45 g. of a violet-black powder with a bronze lustre (Found :* C, 63·7; H, 5·8. $C_{28}H_{30}O_{10}$ requires C, 63·85; H, 5·75%). The acetate is soluble in acetone, acetic acid and chloroform and slightly soluble in ether and water. In all solvents except ether it dissolves with a very intense violet colour. When the colourless ethereal *solution is shaken with water, this slowly becomes coloured.*

The *perchlorate*, prepared from perchloric acid and the acetate in chloroform–ether solution, crystallises in violet leaflets with an intense metallic lustre. It decomposes violently when heated. For analysis the compound was oxidised with acid potassium permanganate, and the perchloric acid then reduced by means of titanous sulphate (Rothmund, *Z. anorg. Chem.*, 1909, **62**, 108) (Found : Cl, 6·1. $C_{26}H_{27}O_{12}Cl$ requires Cl, 6·3%).

2′ : 4′ : 6′-Trimethoxyphenylphthalide (III).—Hydrogen chloride was passed into a solution of phloroglucinol trimethyl ether (1·1 g.) and *o*-phthalaldehydic acid (0·5 g.) in absolute alcohol (15 c.c.); *colourless crystals were soon deposited. The product (1·1 g.) was* collected after 12 hours and recrystallised from alcohol and from toluene; m. p. 200° (corr.) (Found : C, 67·9; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·4%). The production of the phthalide is in agreement with the facts that alcoholic hydrogen chloride splits off one molecule of phloroglucinol trimethyl ether from the compound (IV) and that benzhydrol-*o*-carboxylic acids very readily lose water, yielding phthalides.

Phloroglucinolphthalein Hexamethyl Ether (IV).—A solution of *phthalyl chloride (2 g.) and phloroglucinol trimethyl ether (3·3 g.)* in absolute ether containing freshly fused zinc chloride (about 8 g.) was shaken during 15 minutes. The slightly coloured ethereal layer was then poured off, the violet residue decomposed by water, and the solid separated. After being washed with water, ground with excess of potassium hydroxide solution, again washed, and dried (yield, 4·2 g.), it was recrystallised from alcohol and from toluene; it was then colourless and melted at 175—176° (corr.) (Found : C, 66·6; H, 5·7. $C_{26}H_{26}O_8$ requires C, 66·9; H, 5·6%). It forms a violet solution in dilute hydrochloric acid.

The phthalein (IV), dissolved in hot alcohol, was treated with concentrated hydrochloric acid, and when the violet colour had been discharged the solution was evaporated to a small volume, treated with an excess of aqueous potassium hydroxide to hydrolyse the ester formed, and acidified. 2′ : 4′ : 6′-*Trimethoxybenzoyl*-o-*benzoic acid* was precipitated; after recrystallisation from water and from toluene, it melted at 184—185° (corr.) (Found : C, 64·4; H, 5·0; equiv., 320. $C_{17}H_{16}O_6$ requires C, 64·5; H, 5·1%; equiv., 316).

The phthalein (0·5 g.), dissolved in 5 c.c. of glacial acetic acid, was boiled with 1 c.c. of hydrochloric acid for a few minutes until the violet colour had disappeared. Addition of water then precipitated phloroglucinol trimethyl ether (0·31 g.; calc., 0·36 g.). The filtrate contained phthalic acid.

Resorcinolphthalein Tetramethyl Ether (V).—This compound, which could not be prepared from phthalyl chloride and resorcinol dimethyl ether, was made in the following way : A solution of 2′ : 4′-dimethoxybenzoyl-*o*-benzoic acid (3 g.) in hot resorcinol dimethyl ether (3 g.) was cooled and treated with a cold solution of 10 c.c. of concentrated sulphuric acid in 20 c.c. of anhydrous ether. The mixture was poured into 300 c.c. of cold water, the ether expelled by heating on the steam-bath, and the water decanted from the viscous reaction product. This, after being freed from the excess of resorcinol dimethyl ether by steam-distillation, solidified on cooling (yield, 4·1 g.) and was then recrystallised from alcohol and from toluene; it crystallised very slowly (Found : C, 70·8; H, 5·4. $C_{24}H_{22}O_6$ requires C, 70·9; H, 5·5%). This colourless compound, m. p. 153° (corr.), is soluble without colour in acetone, acetic acid and hot alcohol. In 20% hydrochloric acid it dissolves with a reddish-violet colour.

Phenolphthalein Monomethyl Ether (VI; R = C_6H_4·OMe).—(1) Phenolphthalein (1 mol.) was treated with methyl sulphate (1 mol.), and the crude product was dissolved in ether and repeatedly shaken with sodium carbonate solution, until this remained colourless (about 15 times). The monomethyl ether was now extracted from the ethereal solution by means of *N*-sodium hydroxide, recovered by acidification, and crystallised from benzene and from toluene.

(2) 4′-Methoxybenzoyl-*o*-benzoic acid (3 g.) and phenol (3 g.) were fused together and cooled, a solution of concentrated sulphuric acid (12 c.c.) in anhydrous ether (12 c.c.) added, and the mixture poured into cold water. The purification was as described above, but three washings with sodium carbonate were sufficient to remove unchanged acid and the trace of phenolphthalein formed. The yield of monomethyl ether was 3·1 g. (80%).

A specimen recrystallised from toluene, when dried at 130° in a current of air under diminished pressure, lost 12·2% in weight (calc. for ½ molecule of toluene of crystallisation, 12·3%).

Resorcinolphenolphthalein 2′ : 4′-Dimethyl Ether [VI; R = $C_6H_3(OMe)_2$].—4′-Hydroxybenzoyl-*o*-benzoic acid (2 g.) was dissolved with cooling in 10 c.c. of concentrated sulphuric acid and added slowly to a solution of resorcinol dimethyl ether (1·5 g.) in 20 c.c. of anhydrous ether, and the whole was poured into water. The mixture was then extracted with ether. The ethereal solution was washed twice with potassium bicarbonate solution, whereby the unchanged acid, if any, was removed. Two extractions with 50 c.c. of *N*-sodium hydroxide brought the *phthalein* into aqueous solution. This was freed from ether by warming on the steam-bath, cooled, and acidified. After recrystallisation from alcohol the phthalein melted at 220° (corr.). For combustion it was recrystallised from toluene (Found: C, 73·2; H, 4·9. $C_{22}H_{18}O_5$ requires C, 72·9; H, 5·0%).

Phloroglucinolphenolphthalein 2′ : 4′ : 6′-Trimethyl Ether [VI; R = $C_6H_2(OMe)_3$].—This was prepared from 1·4 g. of phloroglucinol trimethyl ether and 2 g. of the ketonic acid in the same way as the previously described compound. Yield, 1·15 g.; m. p. 200° (corr.) (Found: C, 70·2; H, 5·2. $C_{23}H_{20}O_6$ requires C, 70·4; H, 5·1%).

In this case an equilibrium seems to be established, ketonic acid + phenolic ether $\rightleftarrows$ phthalein + water, which is displaced towards the left side with increasing sulphuric acid concentration. A certain amount of acid, however, has to be present in order to bring about the condensation. After several experiments the proportion indicated (10 c.c. of acid to 20 c.c. of ether) was found to be the most advantageous in this case.

The phthalein is soluble in sodium carbonate and hydroxide solutions with an intense brownish-yellow colour which is much less readily discharged by excess of alkali than that of the two preceding compounds. The similar colour of a solution in secondary sodium phosphate, however, disappears when a little primary phosphate solution is added.

The author desires to express his gratitude to Professor Einar Biilmann for his kind interest in this work.

UNIVERSITY OF COPENHAGEN. [*Received, March 2nd, 1928.*]

CCV.—*A Quantitative Study of the Oxidation of Methyl Oleate and Elaidate by Hydrogen Peroxide in Presence of Acetic Acid.*

By Thomas Percy Hilditch and Colin Henry Lea.

Böeseken (*Rec. trav. chim.*, 1926, **45**, 842; 1927, **46**, 622) has recently stated that perbenzoic and peracetic acids convert ethylenic groupings into dihydroxylated or glycol residues, but that the mode of action differs with each reagent: perbenzoic acid almost invariably causes the initial production of an oxido- or glycide derivative, $-\overset{\frown O \frown}{CH-CH}-$, whereas peracetic acid and the ethylenic grouping unite to yield the monoacetyl derivative of a glycol:

$$-CH{:}CH- + CH_3{\cdot}CO_2{\cdot}OH \longrightarrow -CH(OH){\cdot}CH(OAc)-.$$

We have observed (J., 1927, 3114) that treatment of an acetic acid solution of unsaturated glycerides with hydrogen peroxide produced glycerides, not only of dihydroxystearic acid, but also of the latter in a monoacetylated form.

As we had in mind the possibility of employing the hydrogen peroxide–acetic acid oxidation as an aid in the study of glyceride constitution, we considered it desirable to make a more thorough examination of the analogous oxidation of methyl oleate and elaidate, which leads ultimately to the formation of the isomeric 9 : 10-dihydroxystearic acids melting respectively at 95° and 132° (Hilditch, J., 1926, 1828).

In order to detect any oxido-compounds present we have followed the procedure of Steger and van Loon (*Rec. trav. chim.*, 1927, **46**, 706), who have shown that oxido-methyl esters are hydrolysed by alcoholic potash in the cold without alteration of the oxido-ring system. The acids thus obtained from the original oxidation product were submitted to systematic fractional crystallisation from ether at 0°, which led to the separation of a very large proportion of the solid acids. In every instance the products obtained by us melted, without purification, within a few degrees of the melting points of the respective dihydroxystearic acids, and far above those of the oxidostearic acids (Table II).

We are therefore convinced that no oxido-compounds result from these oxidations whether carried out at the ordinary temperature or at 95°, but there is, at the same time, definite evidence of the concurrent formation of three types of oxidation product varying in amount according to the temperature of oxidation:—

(i) Simple *dihydroxystearic esters* are produced in appreciable quantities, especially at the lower temperature. They separated from the oxidation mixture as a crystalline deposit and were isolated by crystallisation from acetone at 0°. The yields obtained represent minimum values, since it is quite probable that a small quantity of the dihydroxystearic ester remains behind in the mother-liquor.

(ii) *Acetylated dihydroxystearic esters* are only produced to the extent of about 50% of the total product at room temperature, but in much larger amount as the temperature is increased. The percentage of acetic acid combined in the original oxidised ester was determined, and hence was calculated the total amount of mono-acetylated dihydroxystearic ester present, since we concur with Böeseken (*loc. cit.*) in regarding the formation of partially acetylated derivatives as largely due to the direct addition of peracetic acid to the double bond. (We may state here that the presence of peracetic acid in the reaction mixture was evidenced in all cases by the characteristic odour; also, the opinion that oxidation proceeds by way of peracetic acid is reinforced by our observations that the presence of ferrous or manganous salts markedly retards, instead of accelerating, the oxidation of the unsaturated esters—compounds which tend to reduce peracetic acid restrain the conversion into dihydroxystearic derivatives. Further, although methyl dihydroxystearate is acetylated to some extent when heated at 95° for 4 hours with acetic acid of the net concentration present in the oxidations, this action is by no means sufficient to account for the observed acetyl content of the oxidation products.)

(iii) An *oily product* is also formed—like the dihydroxy-ester, in greater amount at lower temperatures. It has all the properties characteristic of an unsaturated fatty oil or ester which has been exposed to atmospheric oxidation, and in our opinion is largely made up of a compound in which molecular oxygen is held very loosely in direct combination with the unsaturated system. It instantly liberates iodine from acidified potassium iodide solution and on heating to about 100° under reduced pressure froths violently and evolves small quantities of acrid vapour with an acid reaction and the well-known accompanying odour of fatty acids of medium molecular weight. It differs from the ordinary air-oxidised fatty oil in one respect, namely, that after heat-treatment in a vacuum (which also destroys its activity towards acidified iodide solution) it definitely increases in iodine absorption, *i.e.*, a certain proportion of ethylenic compound is regenerated; we are not aware that this early stage of oxygen attachment has yet been observed in the case of air-oxidised films of unsaturated fats.

After hydrolysis of the original product, followed by removal of as much dihydroxystearic acid as possible by solution in ether and subsequent heating at 100° under reduced pressure to remove acetic acid, the oily substance shows no reaction to acid potassium iodide solution and has an apparent saponification equivalent of the order of 220—245; ultimate analysis gave figures in agreement with the addition of two atoms of oxygen per ethylenic linkage [Found : C, 68·4; H, 10·6. Calc. for $C_{17}H_{33}(O_2)\cdot CO_2H$: C, 68·8; H, 10·8%. Calc. for $C_{17}H_{33}(OH)_2\cdot CO_2H$: C, 68·4; H, 11·4%]. In this condition, the material closely resembled in its apparent equivalent and general properties the "neutral oxidised ester" obtained by E. F. Armstrong and one of us (*J. Soc. Chem. Ind.*, 1925, **44**, 44T) as the first stage in the oxidation of methyl oleate by potassium permanganate in acetone solution. It is within our knowledge that a very similar substance results when oleic acid is "blown," *i.e.*, heated in a current of oxygen at about 130—140°; a decline in the rate of absorption of oxygen sets in when about one molecule of the latter has been absorbed per molecule of oleic acid, and the product is a viscid liquid which has an apparently low equivalent, but contains little or no dihydroxystearic acid, and does not break down to any great extent into the normal scission products of disruptive oxidation when submitted to the action of alcoholic alkali.

The formation of this oily residual material in the present instance is therefore most probably conditioned by the relatively slow introduction into the oleate or elaidate molecule of molecular oxygen (produced *in situ* by slow decomposition of some of the hydrogen peroxide) in the form of a very unstable molecular or "peroxide" complex, $-\overset{O_2}{\overbrace{CH-CH}}-$. Its isolation is of some interest from the standpoint of the investigation of "drying" oils, a subject which is, however, too remote from our present theme for further discussion here.

The results may be summed up by saying that, in addition to the last-mentioned compound (which is definitely not a dihydroxystearic acid), oxidation of methyl oleate by hydrogen peroxide in acetic acid leads by two different processes to the exclusive production of derivatives of the same dihydroxystearic acid, m. p. 95°; whereas that of methyl elaidate similarly yields exclusively derivatives of the isomeric form, m. p. 132°. Since Böeseken and Belinfante (*Rec. trav. chim.*, 1926, **45**, 917), using perbenzoic acid, have obtained similar end-products from oleic and elaidic esters, it is clear that whether oxidation proceeds *via* an oxido-compound (perbenzoic acid) or not (hydrogen peroxide in acetic acid) oleates yield the dihydroxy-acid, m. p. 95°, and elaidates give rise to the isomeride,

m. p. 132°. These facts are difficult to reconcile with the view of these workers that inversion takes place during hydration in an acidic medium of the oxido-compound, subsequent to the actual oxidation. They appear rather to afford further cumulative evidence for the view expressed by one of us (J., 1926, 1828) that the acid of m. p. 95°, for example, is produced without intramolecular rearrangement by the oxidation of oleic acid, so that the formation of the isomeric acid of m. p. 132° by alkaline permanganate oxidation of oleic acid must involve an inversion.

This opinion, which is in apparent conflict with the generalisations of Lapworth and Mottram (*Mem. Manchester Lit. Phil. Soc.*, 1927, **71**, 63), has also been criticised by Böeseken and Belinfante (*loc. cit.*) on the grounds that oxidation by permanganate does not normally involve any change of configuration. The latter objection rather misses the point of the suggestion made in the earlier communication, namely (*loc. cit.*, p. 1830) that "inversion" takes place *during oxidation in an alkaline medium.* In order to obtain good yields of dihydroxystearic acid by oxidation of sodium oleate by aqueous permanganate, it is imperative to employ a marked excess of alkali: Lapworth and Mottram (J., 1925, **127**, 1628) recommend the use of equal weights of sodium hydroxide and oleic acid, *i.e.*, about seven times the amount of the former necessary to neutralise the oleic acid. We have had many opportunities from time to time with various acids of the oleic series to confirm the necessity for this precaution, and find that the use of a comparatively slight (*e.g.*, twofold or less) excess causes the production of indefinite and sometimes only semi-solid products. Marked alkaline conditions are, then, essential for the quantitative production of dihydroxystearic acid (m. p. 132°) from oleic acid, or the corresponding (m. p. 95°) acid from elaidic acid.

On the other hand, the opposite isomerides (m. p. 95° from oleic acid and m. p. 132° from elaidic acid) have been exclusively produced by six distinct processes, namely, oxidation *via* the oxido-esters (perbenzoic acid), the direct formation of dihydroxystearic esters and the production of monoacetylated dihydroxystearic esters (present communication), and the three older methods referred to in the previous paper (J., 1926, 1831).

Hence, until rigorous experimental proof to the contrary is available, it appears reasonable to suppose that the dihydroxystearic acid which is formed by so wide a variety of methods is the one more nearly related to the monoethylenic acid from which it emanates.

EXPERIMENTAL.

The methyl oleate and methyl elaidate employed in these experiments were carefully purified specimens prepared as described in the previous communication (J., 1926, pp. 1833, 1834). The same procedure was applied in general to each oxidation, and the experimental data can consequently be presented to a certain extent in a summarised form (Table I).

Oxidation of the Unsaturated Esters.—(i) *At atmospheric temperature.* The ester (20 g.) was mixed with glacial acetic acid (200 c.c.), and a solution of 35% perhydrol (26·5 c.c.) added; the solution remained homogeneous and was set aside for 3 days; further perhydrol (13·5 c.c.) was then added, and the mixture left for a further 7 days at room temperature.

(ii) *At higher temperatures.* A similar solution in acetic acid was placed in a conical beaker immersed in a water-bath which was maintained at 75—80° or 95° in different experiments. Perhydrol (20 c.c.) was added at the commencement, with a further addition of 20 c.c. after 2 hours, after which the mixture was maintained hot for several hours.

At the conclusion of the oxidation, the cooled solution was poured into a cold 7% aqueous ammonia solution (*ca.* 1000 c.c.) with vigorous stirring, after which the product was extracted as rapidly as possible by means of ether. After thorough washing with dilute ammonia and then with water, the oxidised products were recovered from the ether and usually dried finally by heating at 100° in a vacuum for a short time. This procedure led to the regeneration of a certain proportion of unsaturated ester as described on p. 1577, and it was necessary, in order to determine the degree of unsaturation of the oxidised material, to dry the ethereal solution over anhydrous sodium sulphate and remove the last traces of solvent under reduced pressure at as low a temperature as possible.

The changes accompanying the increase in iodine value on heating under reduced pressure included the evolution of small quantities of vapour which possessed an acrid odour and an acid reaction to litmus paper, but which did not attack starch-iodide paper (absence of peracetic acid); the consequent loss in weight was small.

In order to eliminate the possibility of error through retention of hydrogen peroxide by the ester, a "blank" oxidation was carried out on a specimen of methyl palmitate with the following results:—

	Iodine value.	Starch-iodide test.
Original ester	0·5	—
After oxidation, dried at 40° for 7 minutes *in vacuo*	0·6	Slight +ve.
After oxidation, dried at 100° for 2 hours *in vacuo*	0·9	Negative.

TABLE I.

Oxidation of methyl oleate and elaidate (20 g.) *at various temperatures.*

No.	Ester oxidised.	Temp.	Time.	Oxidised ester.		Iodine value.		Mean saponification equivalent.
				Wt.	Appearance.	Dried *in vacuo* below 45°.	After 100° *in vacuo*.	
1	Methyl oleate.	15—20°	10 days	20·5	Very soft, semi-solid.	2·9	11·4	231·5
2	,, ,,	75—80	9 hours	19·2	Pale-coloured oil, containing quantities of crystalline material.	Not estd.	5·9	208·1
3	,, ,,	95	4½ ,,	19·2		−0·7	4·8	203·7
4	Methyl elaidate	15—20	10 days	20·0	Somewhat soft, solid mass.	Not estd.	11·1	225·1
5	,, ,,	95	4½ hours	16·8	Solidified rapidly.	0·8	4·9	202·6

TABLE II.

No. of expt.	Dihydroxy-ester isolated.		Acetyl content.		Solid acids obtained				Deficit* of dihydroxy-acid, %.	Oily residue.	
					from separated salts.		from solution.				
	%.	M. p.	$CH_3·CO$, %.	As mono-acetyl ester, %.	%.	M. p.	%.	M. p.		%.	Sap. equiv.
1	15	62— 63°	6·4	56	35·0	88— 89·5°	19·0 3·2	83— 85° 83— 85	13	42	245·6
2	—	—	8·2	71	43·7	87— 89	18·0 3·8	81— 84 73— 76	?	35	247·1
3	6	63— 65	8·9	77	44·0	88— 89	16·8 5·8	79— 81 79— 81	16	30	—
4	22	98— 99	5·4	46	50·2	125—126	12·5	122—123	6	37	210·0
5	12	100—101	8·2	71	56·4	125—126·5	14·8	120—122	15	29	228·8

* The deficit is probably due in part to dihydroxy-acid retained in the oily product. Some diacetylated ester may also be produced by subsequent acetylation of the hydroxy-esters.

There was no frothing or evolution of acid vapour when the recovered ester was heated at 100° under reduced pressure.

Some parallel experiments were also made with two methyl esters consisting of mixtures of oleate and linoleate which had been stored for some time with partial access to air. Each gave a definite starch–iodide reaction and possessed the typical oxidised oil odour; the heat treatment caused a brief effervescence similar to that observed with the esters which had been treated with hydrogen peroxide, the evolved vapour being acid to litmus, whereas after heating the products ceased to liberate iodine from acidified iodide solution. The behaviour of the slightly air-oxidised esters was thus qualitatively parallel with those studied in the present work, but no definite alteration in their iodine values was observed after the heat treatment; apparently the absorbed oxygen, although still reactive to hydrogen iodide, was more firmly combined than in the oily part of the products obtained with hydrogen peroxide.

Separation of Free Dihydroxystearic Esters.—Portions of the original oxidised esters from experiments 1, 3, 4 and 5 were treated with a little acetone and set aside at 0° for some days; the crystalline deposit was filtered off and washed with a little cold acetone and the filtrates and washings were concentrated and again cooled at 0°. The weights and melting points (without further purification) of the successive crops are given in Table II.

The mixed solids separated from the oleate oxidations melted at 66—68° when mixed with methyl 9 : 10-dihydroxystearate (m. p. 70—71°), and the similar products from the elaidate melted at 102—102·5° on admixture with the isomeric methyl 9 : 10-dihydroxystearate (m. p. 105°); a single crystallisation of either group of esters furnished specimens which melted respectively at 69—70·5° and 103—103·5°. It is thus clear that the compounds in question were free dihydroxystearic, and not oxido-, esters.

Estimation of the Proportion of Acetylated Ester present.—Following the determinations of saponification equivalent on the original products, the solvent alcohol present was removed and the residue made acid with 2*N*-sulphuric acid (about 10 c.c. excess), after which it was distilled in steam until all acetic acid had been removed; the condensates were then titrated in the usual way.

In order to ascertain how far the presence of acetylated ester was due to acetylation of methyl dihydroxystearate, rather than to the intervention of peracetic acid, methyl 9 : 10-dihydroxystearate (m. p. 105°; 3·5 g.) was heated at 95° with a mixture of glacial acetic acid (30 g.) and water (6 g.) for 4 hours; the recovered product melted at about 95° [Found: sap. equiv., 278·4. Calc. for $C_{17}H_{33}(OH)_2\cdot CO_2Me$

330. Found: $CH_3 \cdot CO$, 2·8%]. Acetylation had therefore occurred to the extent of about 24% (as monoacetyl derivative).

Hydrolysis of the Oxidised Esters and Separation of Dihydroxystearic Acids from the Oily Residue.—The original oxidised esters (*ca.* 15 g.) were mixed with cold *N*/2-alcoholic potash (200 c.c.) and left at room temperature for 17—18 hours, followed by a period of 6—7 hours at 0°. A considerable deposit of crystalline potassium salt was acidified separately, and the melting point of the recovered acid determined without further purification. The acids recovered from the soluble potassium salts were separated from the oily product by crystallisation from 70% alcohol and finally from ether at 0° (compare Table II).

The melting points, even of the less pure fractions, are far above those given by Böeseken and Belinfante (*loc. cit.*) for the 9 : 10-oxidostearic acids (52° and 60—61°, respectively). The melting points of mixtures of the respective products, as obtained, with the appropriate 9 : 10-dihydroxystearic acid were 89·5—90·5° in the case of the oleate products and 127—128° in that of acids from methyl elaidate.

Examination of the Oily Residues.—The general properties of these products (which were similar in each case, except that those from methyl elaidate were more viscous than those from methyl oleate) have already been dealt with (p. 1577).

THE UNIVERSITY, LIVERPOOL. [*Received, March 14th*, 1928.]

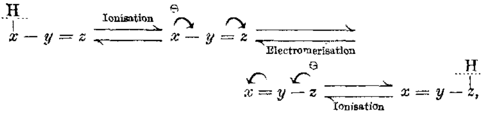
CCVI.—*The Mechanism of Tautomeric Interchange and the Effect of Structure on Mobility and Equilibrium. Part II. Ring-Chain Tautomerism in its Relation to the Mutarotation of the Sugars.*

By JOHN WILLIAM BAKER.

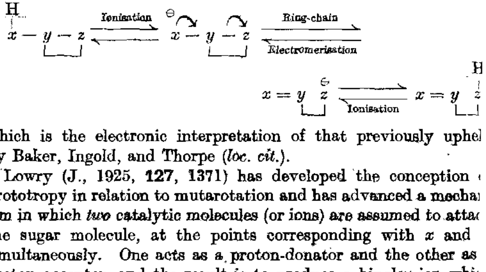
IN view of the correlation which has heen established [E. H. Ingold (Usherwood), *Chem. and Ind.*, 1923, **42**, 1246; Cooper, Ingold, and Ingold, J., 1926, 1868] between triad tautomerism, ring-chain tautomerism, and additive reactions (as keto-enol change, keto-cyclol change, and the aldol reaction), the inclusion of the chemical transformations underlying the mutarotation of sugars within the general phenomenon of ring-chain tautomerism Jacobsen and Stelzner, Meyer and Jacobsen's "Organische Chemie," 2 Afl., 1, 2, pp. 886, 910, 915, 927; Baker, Ingold, and Thorpe, J., 1924, **125**, 268) has paved the way for the application of new analogies. There is, in fact, no reason to doubt that the mutarot-

ation of sugars is dependent on prototropy (compare Kuhn and Jacob, *Z. physikal. Chem.*, 1924, **113**, 389; Lowry, *Chem. Rev.*, 1927, **4**, 231) and not on anionotropy, that is, a phenomenon analogous to that exhibited by pseudo-bases.

Ingold, Shoppee, and Thorpe (J., 1926, **1477**) have examined the effect of structural influences on triad prototropy on the basis of the mechanism



the assumed function of catalysts being the facilitation of th preliminary ionisation. This paper contains a study of structura effects on ring-chain tautomerism in its application to the muta rotation of sugars, and the results are considered in the light of th corresponding mechanism

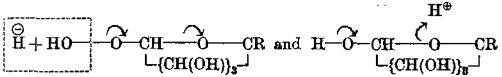


which is the electronic interpretation of that previously uphel by Baker, Ingold, and Thorpe (*loc. cit.*).

Lowry (J., 1925, **127**, 1371) has developed the conception o prototropy in relation to mutarotation and has advanced a mecha ism in which *two* catalytic molecules (or ions) are assumed to atta the sugar molecule, at the points corresponding with x and simultaneously. One acts as a proton-donator and the other as proton acceptor, and the result is to produce a bipolar ion whi undergoes internal neutralisation with a change of structure. Th theory of duplex action differs from the above theory of unitary acti in certain consequences, some of which will be considered below.

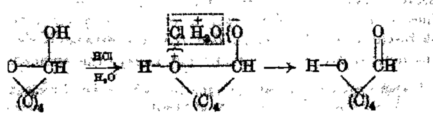
The *detailed consideration* of the mechanism divides itself in two parts: the history of the ionised proton and the history of t electrons from which it separates; or, in other words, the functio of catalysts, and the function of structural influences in the sug molecule. Catalysts are expected to be of two kinds: (i) tho which attack the ionising proton directly, such as the anions weak acids, water, and all other bases; (ii) those which facilita its liberation indirectly, such as the cations of weak bases, wat

and all other acids. The respective mechanisms may be represented by the examples :



and in the second illustration it is not necessary to suppose that the attacking proton is free or that the eliminated one remains in that condition; nor does the illustration represent the only possible method of indirect action, another type of which is elaborated below (p. 1586). The essential function of a catalyst of this class is regarded as that of bringing a positive potential into the molecule in positions which will facilitate the electromeric changes necessary to the reaction. The nature of the sugar molecule itself is of importance in this connexion. Glucose is a definite, although very weak, acid ($k = 3{\cdot}6 \times 10^{-13}$) and should obviously be capable of catalysing its own mutarotation, either through its anion by the first of the mechanisms indicated, or by means of the molecule according to the second mechanism. Dawson's work has shown that catalytic coefficients differ by enormous ratios, and it would therefore be dangerous to conclude that the "arrests" of mutarotation observed (Lowry and Richards, J., 1925, **127**, 1385) in organic solvents at the ordinary temperature demonstrate a condition *qualitatively* different from the ordinary dynamic condition of a dissolved sugar which has not attained equilibrium. Evidence is recorded in this paper indicating that specimens of tetramethyl- and tetra-acetyl-glucose, which show an "arrest" in purified solvents at the ordinary temperature and even at 44°, mutarotate rapidly at a suitable higher temperature; in particular, in the fused condition in silica apparatus, the cleanliness of which had previously been demonstrated by the repeated production of "arrests." These results completely confirm the work of Irvine and Gilmour (J., 1908, **93**, 1440) on the relative nature of so-called arrests, and favour the inclusion of the sugars themselves within the category of catalysts, as is required by the theory of mechanism indicated above.

Turning to structural influences, Lowry's theory of duplex catalytic action is expressed as follows, simultaneous attack by an acid and water being taken as an example :



and a similar mechanism presumably applies to the mutarotating nitrogen sugars in which the ·OH group of the cyclol form is replaced by NHR. In these compounds the group R can, of course, be varied, and the facility of the change would thus appear to depend on the extent to which it collaborates with the proton acceptor. This may be deduced from the strengths as acids of the compounds $R·CO_2H$ or R·OH, and for the groups R indicated should be as follows:

$$C_6H_4Br(Cl)(p) > C_6H_5 > C_6H_4Me(p) > C_6H_4·OMe(p)$$

On the other hand, the mechanism derived from analogy with triad tautomerism presumes that the attack of an acid catalyst would be indirect and would operate at the most basic part of the molecule, and thus the strengths as bases of the compounds $R·NH_2$ or $R·NR^1R^2$ should determine the relative velocities of isomerisation, a sequence which is the reverse of that given above:

$$C_6H_4·OMe(p) > C_6H_4Me(p) > C_6H_5 > C_6H_4Cl(p) > C_6H_4Br(p)$$

The experimental results which relate to a series of nitrogen sugars, prepared from tetra-acetylglucosidyl bromide, correspond with this deduction. The strengths of the five primary bases $R·NH_2$ vary over a range of 1 : 15, and the coefficients for the velocities of mutarotation of the corresponding sugars under constant conditions of temperature and acid catalysis vary as 1 : 23, but the ratios of the two constants are grouped in a striking manner round a common value (p. 1593).

An unexpected point of considerable interest has emerged during the study of sugars derived from secondary bases. If the attack of the acid catalyst on one of the sugars considered in the preceding paragraph were to result in actual co-ordination of a proton to give an ammonium complex which then became the actual individual responsible for mutarotation, it is evident that, since the nitrogen atom in the latter would bear two equivalent hydrogen atoms, the replacement of one of them by methyl should not fundamentally affect the situation, because the other still remains available to act as the mobile hydrogen atom. Tetra-acetylglucosemethylanilide was prepared and examined, but no signs of mutarotation could be detected, either at the ordinary temperature under conditions varying from those conducive to "arrests" to those in which considerable concentrations of acid were employed, or in the fused state. It is concluded that the attack of the catalyst does not involve co-ordination,* but merely the augmentation of

* This may not necessarily be the case with sugar derivatives of very strong bases, examples of which are at present under investigation.

the positive field in the region of the electrons binding the original hydrogen atom by an electrostatic mechanism which may be correlated with the modern theory of electrolytes. In short, it is the hydrogen atom already present in the system H—X—C—O—C which is the mobile one, and the recognition of this circumstance by Baker, Ingold, and Thorpe was one of the principal reasons for grouping mutarotation phenomena within the general category of ring-chain tautomeric changes. The stronger the basic properties of the unshared nitrogen electrons, the closer will the polar reagent approach: the greater the field thus induced, the smaller will be the reaction of the valency electrons on the nucleus of the mobile hydrogen. Thus the effect of structural changes on the velocity of mutarotation should run parallel with their effect on basic character, as is found to be the case.

In the absence of acid catalysts, however, it is obvious from the scheme given on p. 1584 that the velocity of mutarotation should depend on the tolerance of the atom x (from which in the cyclol form the proton separates) for a negative charge, and hence, under such conditions, it is to be expected that the velocity of mutarotation should be greater when x is an oxygen atom than when it is nitrogen. This is actually the case. The velocity coefficient of tetra-acetyl glucose (H—O—C—O—C) in 90% alcohol at 44° is 1·07 $hrs.^{-1}$, whereas in the same solvent at the same temperature the velocity of mutarotation of tetra-acetylglucoseanilide (H—N—C—O—C) is too slow to measure, the initial value $[\alpha]^{44°}_{5461}$ −73·7° being unchanged after 24 hours. Mutarotation of the anilide does, however, proceed fairly rapidly in the fused condition: a sample which had m. p. 98° and $[\alpha]^{24°}_{5461}$ −75·2° in "arrest" ethyl acetate, had m. p. 60° and $[\alpha]^{24°}_{5461}$ +45·7° in the same solvent after previous heating at 100—105° for 1 hour.

The matter will be developed further in future papers.

EXPERIMENTAL.

I. *Experiments on "Arrest" Specimens.*

A. *Materials used.*—A pure specimen of tetra-acetyl *d*-glucose supplied by Messrs. Boots Pure Drug Co. was dried for 12 months over phosphoric oxide in a vacuum desiccator. A specimen of tetramethyl glucose, m. p. 80°, prepared by The British Drug Houses, Ltd., was rapidly crystallised from a mixture of pure dry ether and ligroin (b. p. 30—40°) with the rigid exclusion of moisture. The process was repeated until a product of m. p. 103—104° (speci-

men put into a bath at 90° initially) was obtained. This specimen was stored over phosphoric oxide in a vacuum for 18 months without any change of m. p. being detected. Ethyl acetate was purified in the usual manner and finally distilled twice over phosphoric oxide. The latter operation seemed to give the sample a very slight acid reaction, and a better specimen was obtained by subsequent treatment with a little dry sodium, followed by slow distillation (twice) in a carefully purified apparatus made of pyrex glass throughout and protected from atmospheric moisture. The acetone used was purified through the sodium iodide compound by the method of Shipsey and Werner (J., 1913, **103**, 1255) employed by Lowry.

B. *Description of Apparatus.*—The apparatus, which was composed entirely of clear fused silica, consisted of a 2-dcm. polarimeter tube, 1 cm. in diameter, with optically ground end-plates fused on. At a distance of 2 cm. from each end were fused in two side-tubes, 0·5 cm. in diameter, bent at right angles and connected by ground joints to two flasks of about 25 c.c. capacity, each of which had a wide fused-in side-tube bent at right angles. In this side-tube a small glass tube containing phosphoric oxide could be placed (thus making it possible to replenish the drying agent without soiling the side-tube with phosphoric acid) and it was connected during the actual arrest experiment to a large backing train of phosphoric oxide drying-tubes. The whole apparatus was constructed to specification by the British Thermal Syndicate, Newcastle. The apparatus was initially purified by prolonged steaming and dried by heating in a slow current of air (dried by phosphoric oxide) at reduced pressure. Subsequently, cleaning was effected simply by washing with the pure "arrest" solvent and drying in a stream of dry air.

The polarimeter tube was jacketed for temperature control. The temperature readings recorded are those of the jacket of the tube. Readings were made for the mercury green line, the source of light being a powerful Kelvin, Bottomley and Baird mercury vapour lamp.

Arrest of Mutarotation.—(a) *Tetra-acetyl glucose in ethyl acetate.* A solution containing 1·343 g. in 100 c.c. at 24° had α +0·18°, ($[\alpha]^{24°}_{5461}$ 6·7°), unchanged for 23 hours. Thereafter, very slow mutarotation occurred, but it was not complete when observations were stopped (171 hours; α +1·82°).

(b) *Tetramethyl glucose in ethyl acetate.* A solution containing 1·526 g. in 100 c.c. at 44° had α +4·34° ($[\alpha]^{44°}_{5461}$ 142·3°), unchanged for 6 hours. This value is considerably higher than that ($[\alpha]_{5461}$ 122·4°) recorded by Lowry (*loc. cit.*) in agreement with the higher

m. p. of the sample used. Mutarotation then proceeded slowly and was complete in about 198 hours.

(c) *Tetramethyl glucose in acetone.* A solution containing 1·482 g. in 100 c.c. had at 44° α +4·02° ($[\alpha]_{5461}^{44°}$ 135·6°), unchanged for over 3 hours, after which slow mutarotation set in.

C. *Mutarotation in the Fused State.—Tetra-acetyl glucose.* Fusion of the sugar (0·249 g.) at 130—135° for 30 minutes was effected in one bulb of the silica apparatus, the other containing the "arrest" ethyl acetate (15·75 g.) ultimately used to test the rotation. Solution was effected by tilting the apparatus. The initial value of α, measured 10 minutes after solution was effected, was 2·12°, whence $[\alpha]_{5461}^{44°}$ = 74·5°. This value remained unchanged for 2 hours, after which the mutarotation was slowly completed, the final constant value ($[\alpha]_{5461}^{44°}$ 91·4°) being reached after 144 hours. The experiment was repeated with similar results.

Tetramethyl glucose. In a similar experiment, this sugar (0·2820 g.) was heated at 120° for 15 minutes in the arrest apparatus and after cooling was dissolved in "arrest" acetone (13·96 g.). The *initial value of α was 3·04°, whence $[\alpha]_{5461}^{41.5°}$ = 95·0°, which remained* unchanged for 24 hours.

II. *Relative Velocity Experiments.*

D. *Preparation of p-Substituted Anilides of Tetra-acetyl Glucose.*—These were obtained by the action of excess of the *p*-substituted aniline on tetra-acetylglucosidyl bromide, a little ether being used as a solvent in the case of the solid bases. The method of isolation varied slightly from case to case, since sometimes the required anilide and sometimes the hydrobromide of the base crystallised.

Anilide. Tetra-acetylglucosidyl bromide (8 g.) was dissolved in 5·6 g. of freshly distilled aniline (3 mols.) and kept for 24 hours at room temperature; precipitation of the partly separated aniline hydrobromide was then completed by addition of ether. The excess of aniline was removed from the filtered ethereal solution by shaking with dilute hydrochloric acid. The residue from the dried ethereal extract slowly crystallised. After several crystallisations from ether–ligroin (b. p. 40—60°) *tetra-acetylglucoseanilide* had m. p. 98° (Found: C, 56·6; H, 6·1. $C_{20}H_{25}O_9N$ requires C, 56·7; H, 6·0%).

The *p-toluidide* was obtained similarly from 8·2 g. of acetobromoglucose and 6·4 g. of *p*-toluidine dissolved in a little ether. After evaporation of the ether on a steam-bath the *p-toluidide* crystallised; after several recrystallisations from methyl alcohol it had m. p. 147° (Found: C, 57·4; H, 6·2. $C_{21}H_{27}O_9N$ requires C, 57·6; H, 6·2%).

p-*Anisidide*. On similar condensation of 8·2 g. of acetobromoglucose with 7·4 g. of *p*-anisidine a mixture of *p*-anisidine hydrobromide and the required anisidide crystallised, from which the latter was separated by crystallisation from aqueous methyl alcohol. A further quantity was obtained from the ethereal extract. After many crystallisations from methyl alcohol–ligroin (b. p. 60—80°) the p-*anisidide* had m. p. 129° (Found: C, 55·6; H, 6·1. $C_{21}H_{27}O_{10}N$ requires C, 55·6; H, 6·0%).

p-*Bromoanilide*. In this case a mixture of *p*-bromoaniline hydrobromide and the required *p*-bromoanilide crystallised. After dilution with ether, the insoluble residue was treated with cold 10% sodium hydroxide solution and extracted with chloroform. *p*-Bromoaniline was removed from the chloroform extract by shaking with dilute hydrochloric acid, and the dried extract concentrated to small bulk. On addition of ligroin and seeding, the product crystallised. A further quantity was obtained in the usual manner from the ethereal extract. After several crystallisations from pure methyl alcohol the p-*bromoanilide* had m. p. 160° (Found: C, 47·9; H, 4·9. $C_{20}H_{24}O_9NBr$ requires C, 47·8; H, 4·8%).

The p-*chloroanilide* was prepared in a similar manner. After many crystallisations from methyl alcohol–ligroin (b. p. 60—80°) it had m. p. 147° (Found: C, 52·1; H, 5·4. $C_{20}H_{24}O_9NCl$ requires C, 52·5; H, 5·3%). It is much more soluble in methyl alcohol than the *p*-bromo-compound.

N-*Methylanilide*. A mixture of acetobromoglucose (8·0 g.) and 6 g. of freshly distilled methylaniline (3 mols.) was warmed on the steam-bath to effect solution. After standing for 6 hours, it was again warmed on the steam-bath for 5 minutes to complete the reaction. The resulting dark green, viscous gum was largely diluted with dry ether, and the precipitated methylaniline hydrobromide filtered off. The ethereal extract was shaken with dilute hydrochloric acid, which removed the excess of methylaniline and nearly all the colour. The pale yellow syrup obtained from the dried ethereal solution slowly crystallised in a vacuum desiccator. After several crystallisations from ether–ligroin, the N-*methylanilide* had m. p. 102° (Found: C, 57·7; H, 6·5. $C_{21}H_{27}O_9N$ requires C, 57·7; H, 6·2%).

E. *Mutarotation in* 90% *Alcohol*.—The solvent used was prepared by the addition of 10% (by weight) of conductivity water to pure absolute alcohol, which had been carefully distilled several times. The water was added in order to prevent relatively large changes in the water content of the solvent owing to the hygroscopic character of absolute alcohol.

(a) *Tetra-acetyl glucose.* Strength of solution, 2·0956 g./100 c.c. Temp., 44°.

Time (hrs.).	α.	$[\alpha]_{5461}$.	k (hrs.$^{-1}$).	Time (hrs.).	α.	$[\alpha]_{5461}$.	k (hrs.$^{-1}$).
0·183	+1·06°	25·3°	—	0·913	+2·59°	61·8°	1·0709
0·23	1·22	29·1	(0·9488)	1·0	2·68	63·9	1·0534
0·25	1·31	31·2	(0·9970)	1·166	2·86	68·2	1·0320
0·283	1·39	33·1	1·0720	1·416	3·11	74·2	1·0766
0·333	1·54	36·7	1·1241	1·50	3·15	75·1	1·0966
0·416	1·71	40·8	1·0993	1·75	3·32	79·2	1·0684
0·50	1·89	45·1	1·0598	2·0	3·42	81·6	1·0442
0·583	2·05	48·9	1·0569	2·50	3·62	86·4	—
0·666	2·21	52·7	1·0654	3·50	3·79	90·4	—
0·75	2·35	56·0	1·0681	∞	3·97	94·7	—
0·833	2·48	59·1	1·0718			Mean	1·067

(b) *Tetra-acetylglucoseanilide.* A solution containing 1·5188 g. in 100 c.c. had $[\alpha]_{5461}^{24°}$ − 73·7°, unchanged after 24 hours. Evaporation of this solution over phosphoric oxide in a vacuum at the ordinary temperature yielded a pure white solid, m. p. 97°, showing that the original material was unchanged.

Mutarotation of tetra-acetylglucoseanilide on fusion. A sample of the anilide having m. p. 98° and $[\alpha]_{5461}^{24°}$ − 75·2° in "arrest" ethyl acetate was heated at 105—110° for 1 hour and then cooled. The product had m. p. (indefinite) about 60°; and a solution containing 0·7512 g. in 100 c.c. gave α + 0·69°, whence $[\alpha]_{5461}^{24°}$ = + 45·7°, mutarotation having occurred during fusion.

Comparative Velocities of Mutarotation of Tetra-acetylglucoseanilides in Ethyl Acetate with Acid Catalysts at 24°.—Since it was only desired to determine the relative velocities of mutarotation of the anilides in the same solvent under the same conditions of catalysis, the solvent used was prepared empirically by addition of such small amount of hydrochloric acid to ethyl acetate as gave conveniently measurable velocities. The ethyl acetate used contained a little acetic acid (S), but it was shown that the catalytic activity of the acetic acid was only of the order of 1—2% of that produced by an equivalent concentration of hydrochloric acid. The order of the velocities of mutarotation was confirmed, for three of the five derivatives, in pure ethyl acetate to which only acetic acid in concentration 0·9*N* had been added (U). In certain cases, the standard catalytic solution was diluted with pure ethyl acetate (T) in order to reduce the velocities of mutarotation to measurable magnitudes, the two series of measurements being correlated by a determination of the velocity of mutarotation of the anilide in both solvents.

The value of $[\alpha]_0$ was obtained graphically by extrapolation of

the straight line obtained by plotting $\log([\alpha]_\infty - [\alpha]_t)$ against t. Details of the optical measurements are recorded only in the first example.

*Mutarotation of tetra-acetylglucose-*p*-bromoanilide in S*: strength of solution, 1·1668 g./100 c.c. (0·0233 g.-mol./l.). $k = \frac{2{\cdot}3}{t} \log \frac{[\alpha]_\infty - [\alpha]_0}{[\alpha]_\infty - [\alpha]_t}$ hrs.$^{-1}$.

Time (t hrs.).	a.	$[\alpha]_{5461}$.	k.	Time (t hrs.).	a.	$[\alpha]_{5461}$.	k.
0·033	−1·11°	−47·55°	2·258	0·833	+0·50°	+21·42°	2·025
0·083	*0·96*	*41·13*	*1·835*	*0·917*	*0·55*	*23·57*	*1·986*
0·166	0·68	29·14	1·890	1·00	0·60	25·71	1·974
0·25	*0·40*	*17·14*	*2·039*	*1·25*	*0·70*	*29·99*	—
0·333	0·21	9·00	2·003	1·75	0·82	35·14	—
0·417	*0·02*	*0·86*	*2·050*	*2·50*	*0·88*	*37·70*	—
0·50	+0·10	+ 4·29	1·990	3·75	0·89	38·14	—
0·533	*0·22*	*9·43*	*2·172*	∞	0·90	38·56	—
0·699	0·40	17·57	2·115			Mean	2·028

*Tetra-acetylglucose-*p*-chloroanilide in S*: strength of solution 1·0012 g./100 c.c. (0·0219 g.-mol./l.). Mean value of k (11 observ ations), 2·77 hrs.$^{-1}$ ± 0·07.

Tetra-acetylglucoseanilide in S: strength of solution, 1·0092 g. 100 c.c. (0·02385 g.-mol./l.). Mean value of k (9 observations) 7·77 hrs.$^{-1}$. Maximum, 8·09; minimum, 7·21.

Tetra-acetylglucoseanilide in T: strength of solution, 1·0212 g. 100 c.c. (0·0242 g.-mol./l.). Mean value of k (12 observations) 4·06 hrs.$^{-1}$. Maximum, 4·34; minimum, 3·89.

*Tetra-acetylglucose-*p*-toluidide in T*: strength of solution, 0·841 g./100 c.c. (0·0193 g.-mol./l.). Mean value of k (6 observations 15·6 hrs.$^{-1}$. Maximum, 17·6; minimum, 14·2.

*Tetra-acetylglucose-*p*-anisidide in T*: strength of solution, 1·028 g./100 c.c. (0·0227 g.-mol./l.). Mean value of k (8 observations 24·3 hrs.$^{-1}$. Maximum, 26·3; minimum, 22·4.

Mutarotation in ethyl acetate 0·9N *with respect to acetic acid* (U. (a) *Tetra-acetylglucoseanilide*: strength of solution, 0·9408 g 100 c.c. Mean value of k (11 observations), 0·209 hrs.$^{-1}$. Maximum 0·248; minimum, 0·188.

(b) *Tetra-acetylglucose-*p*-toluidide*: strength of solution, 1·02 g./100 c.c. Mean value of k (10 observations), 0·577 hrs.$^{-1}$. Maximum, 0·604; minimum, 0·543.

(c) *Tetra-acetylglucose-*p*-anisidide*: strength of solution, 0·98 g./100 c.c. Mean value of k (9 observations), 1·69 hrs.$^{-1}$. Maximum, 1·88; minimum, 1·55.

Summary of Results.

Relative velocities of mutarotation of para-substituted anilides of tetra-acetyl glucose with acid catalysis (K_b is the dissociation constant of the *p*-substituted aniline as a base*).

Substituent.	Anilide (g.-mol./l.).	K_b.	Velocity coefficient of mutarotation, k hrs.$^{-1}$, (*a*) in S.	(*b*) in T.	(*c*) in U.	k/K_b (for S).
Br	0·023	$1·0 \times 10^{-10}$	2·00	—	—	)$2·0 \times 10^{10}$
Cl	0·022	$1·5 \times 10^{-10}$	2·74	—	—	$1·83 \times 10^{10}$
H	0·024	$4·6 \times 10^{-10}$	7·76	4·05	0·209	$1·69 \times 10^{10}$
Me	0·020	$11—15 \times 10^{-10}$	(29·6)†	15·45	0·577	$1·97 \times 10^{10}$
OMe	0·023	15×10^{-10}	(45·9)	23·92	1·69	$3·06 \times 10^{10}$

Attempt to cause Tetra-acetylglucose-N-methylanilide to exhibit Mutarotation.—(a) *In "arrest" ethyl acetate.* A solution containing 1·0224 g. in 100 c.c. had $[\alpha]_{5461}^{24°}$ +49·0°, which remained unchanged for 24 hours, even after the addition of a trace of hydrochloric acid on a platinum wire. The residue obtained by evaporating this solution over phosphoric oxide at the ordinary temperature had m. p. 95—96° without purification.

(b) *In ethyl acetate containing hydrochloric acid.* A solution of 1·0380 g. in 100 c.c. of ethyl acetate about 0·03*N* with respect to acid had $[\alpha]_{5461}^{24°}$ + 51°, and one containing 1·040 g. in 100 c.c. with only about 1/10 this concentration of acid had $[\alpha]_{5461}^{24°}$ + 52·5°, both values being constant.

(c) *On fusion.* A sample of the methylanilide was heated at 105—110° for a short period and cooled. A solution containing 1·0432 g. in 100 c.c. in "arrest" ethyl acetate had $[\alpha]_{5461}^{24°}$ + 51·8°. In no case could any change in rotation be observed.

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THE UNIVERSITY, LEEDS. [*Received, March 15th, 1928.*]

* From Landolt-Börnstein. The values for *p*-toluidine and *p*-anisidine vary, but from theoretical considerations it would be expected that the latter is the stronger base.

† The values in parentheses are extrapolated on the assumption of direct proportionality from those found in *T* by means of the values obtained for the anilide in each solution.

CCVII.—*Electrometric Titration Curves of Dibasic Acids. Part I. Normal Acids.*

By RICHARD GANE and CHRISTOPHER KELK INGOLD.

THE hypothesis that the angles between the valencies of a carbon atom are modified by the space requirements of the attached groups has been attested by chemical evidence of various kinds during the past 13 years, and it therefore seemed desirable to examine the possibility of obtaining confirmation by physical methods. The most hopeful line of inquiry appeared to be to endeavour to establish a connexion between molecular configuration, as determined by the valency-deflexion hypothesis, and the external molecular electrical field, utilising physical properties which are known to depend mainly on this field. Two properties suggested themselves for this purpose, namely, the dielectric constants of dipolar substances and the dissociation constants of acids containing a free pole (*e.g.*, the second dissociation constant of dibasic acids). This paper constitutes a preliminary inquiry into the suitability of the second method of attack.

Bjerrum (*Z. physikal. Chem.*, 1923, **106**, 219) has considered the effect of the external field of a free pole on the active mass of the hydrogen ions in the neighbourhood of a dissociating carboxyl group, and, for the case of a symmetrical dibasic acid, he has calculated from Boltzmann's potential energy–concentration relationship that $\log K_1/K_2 - 0{\cdot}6 = 3{\cdot}1 \times 10^{-8}/r$, where K_1 and K_2 are the first and second dissociation constants of the acid, and r is the distance between the ionising groups. This formula gives values of r which are of the correct order of magnitude (a few Ångstrom units for acids of simple constitution), but the theory is obviously far too simple to warrant the expectation of quantitative accuracy, and even for dilute solutions a complete theory would have to take account *inter alia* of the following factors: (1) The effect of the external field of the pole on hydrogen-ion concentration (Bjerrum), (2) the effect of the external field (the "direct" effect, *D*, see Ingold and Vass, this vol., p. 417) of the pole on the hydrogen-ion affinity of the carboxylate ion, (3) the effect of the internally propagated field ("inductive" and "tautomeric" effects, *I* and *T*) of the pole on the hydrogen-ion affinity of the anion, (4) the influence of electrostriction by the pole of kations and the positive ends of dipolar molecules in diminishing the effects of the pole, as specified under (1), (2), and (3). The neglect of factors (2) and (3) will di[illegible] the apparent distance, *r*, between the carboxyl groups, and

the error arising from the second of these causes will be greater the shorter the intervening carbon chain. On the other hand, the neglect of (4) will render r too large, and for a given degree of electrostriction this effect will be independent of the length of the chain.* In short, it is to be expected that when internally propagated polar factors are negligible, the application of the Bjerrum formula will place a series of substances in the correct order, although the calculated distances between their carboxyl groups will not be physically accurate; when, however, internal factors cannot be neglected, this result will be achieved only for series so chosen that the internal effects are closely comparable. Therefore, as a preliminary to the utilisation of Bjerrum's principle for the purpose referred to at the outset, it seemed desirable to endeavour to determine the region of applicability of the method by the examination of a number of homologues, each of which might conceivably constitute the parent of a series suitable for the investigation of valency deflexion. The parent acids which have been examined are those represented by the general formula $CO_2H{\cdot}(CH_2)_n{\cdot}CO_2H$.

It is well known that the dissociation constant of an acid depends upon the method by which it is measured, that is, on the manner in which concentrations and activities enter into the expression from which it is calculated. Thus the "conductivity" dissociation constant of acetic acid at 18° is $1{\cdot}85 \times 10^{-5}$, whilst values above $2{\cdot}0 \times 10^{-5}$ have been obtained electrometrically. This difference becomes of importance in the application of recorded data to the Bjerrum expression; for whereas K_1 has usually been determined by measurements of the conductivity of the acid, K_2 is exceedingly difficult to evaluate in this way, and has more often been determined by such methods as partition or sugar inversion. Which sort of dissociation constant should theoretically be employed is a remote question, but it seemed to us of greater importance that both K_1 and K_2 should be measured by the *same* method, if possible in the same experiment, and we have therefore employed the mixed activity-concentration constants calculated from electrometric measurements made during neutralisation with a strong base. The theory of the method has been given by Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 65) and is represented by the equation

$$\frac{x}{v} = \frac{K_1C([H^{\cdot}]^2 + 2K_2[H^{\cdot}]) - ([H^{\cdot}]^2 - K_w)([H^{\cdot}]^2 + K_1[H^{\cdot}] + K_1K_2}{([H^{\cdot}]^2 + K_1[H^{\cdot}] + K_1K_2)([H^{\cdot}]^2 + N[H^{\cdot}] - K_w)}$$

where C and v are respectively the initial concentration and volum

* This follows because in the Bjerrum expression the assumed effectiv ionic [illegible] in the form of the ratio e^2/r.

of the solution of acid, and N and x are respectively the concentration and volume of alkali after addition of which the hydrogen-ion concentration is $[H^{\cdot}]$; K_1 and K_2 are the first and second dissociation constants of the acid, and K_w that of water. The expression assumes that the acid is a weak electrolyte and that the base is completely dissociated; it is therefore not applicable to oxalic acid, which does not obey the laws of weak electrolytes in respect of its first dissociation constant.

For the acids $CO_2H\cdot(CH_2)_n\cdot CO_2H$ from malonic acid to azelaic acid, the values of r calculated from the data recorded in the experimental portion are given in the following table. The bottom line shows the deviations from the straight line $r = 4\cdot4 + 1\cdot73n$ to which the observed values for all the acids from glutaric to azelaic closely approximate.

$n =$	1	2	3	4	5	6	7
r (found), Å.U.	1·5	5·0	9·2	11·5	13·2	14·5	16·8
Deviation	−4·6	−2·9	−0·4	+0·2	+0·2	−0·3	+0·3

[The value of r for succinic acid calculated from Auerbach and Smolczyk's electrometric data (*loc. cit.*) is 4·9 Å.U.]

It will be seen that there is no indication of 5-carbon periodicity; this suggests that the polymethylene chain tends to a straight (zigzags) and not a coiled configuration. Further, for these acids the apparent increase in the distance between ionic centres for an increase by one methylene group in the length of the carbon chain is 1·73 Å.U., *i.e.*, it is greater than the distance between the carbon atoms in the diamond (1·52 Å.U.). We are of the opinion that this effect is due largely to the influence of electrostriction which should increase the apparent increment per methylene group by an approximately constant amount throughout the series.

The small deviations shown by the acids from glutaric to azelaic acid may be accounted for as experimental error. Azelaic acid represents the limit of applicability of the method as used by us partly on account of the sparing solubility of sebacic and the higher acids, and partly because the form of the Bjerrum expression renders the calculated values of r more sensitive to experimental error as the series is ascended. Succinic acid, however, shows a negative deviation which far exceeds experimental error, and malonic acid shows a still larger deviation in the same direction. These we attribute to internally propagated polar effects, which naturally become of greater significance the shorter the chain between the carboxyl groups. In malonic acid, moreover, the effect of inductively propagated electronic strain is probably enhanced by incipient [illegible]meric disturbances of the type which has been held responsibl

(Baker, Cooper, and Ingold, this vol., p. 426) for the characteristic thermal decomposition of malonic acids :

$$HO_2C—CH_2—CO—O^{\ominus}$$

As indicated above, it is proposed to make further studies of this kind along the lines prescribed by the foregoing results.

Experimental.

The dibasic acids were either purchased or prepared by known methods, and in all cases carefully purified by repeated crystallisation before use.

The hydrogen-potential measurements were made with accurately calibrated apparatus kindly lent by Messrs. W. R. Atkin and F. C. Thompson of the Leather Industries Department, whose valuable help throughout this work we gratefully acknowledge.

The hydrogen, derived from a cylinder, was purified by passing successively through alkaline permanganate, alkaline pyrogallol, silver nitrate, lead acetate, alkaline permanganate, alkaline pyrogallol, cotton wool, and distilled water. The pole of the hydrogen electrode was re-platinised before each experiment, the direction of the current being reversed every half-minute. A saturated calomel electrode was employed as the second electrode, the two half-cells being connected, through a vessel containing water saturated with potassium chloride and mercurous chloride, by a bridge of saturated potassium chloride containing 1·5% of agar. The potentials were measured on a bridge wire one scale division of which corresponded to 0·1 millivolt, the potential gradient being checked repeatedly by a standard cadmium cell having 1·0183 volts at 20°. All hydrogen-potential measurements were made at 25°. The alkali used was carbonate-free sodium hydroxide, and the solutions of the acids were made up with air-free distilled water immediately before use. All duplicate determinations agreed very closely.

In view of the fact that there is no universally accepted standard of reference for hydrogen potential measurements, we deemed it desirable to correlate our standards with those used by Walpole (J., 1914, **105**, 2501) in his investigation of acetic acid–sodium acetate solutions. Walpole worked at 18° and adopted the Sörensen standard for the decinormal calomel electrode. Our saturated calomel electrode *A*, which was selected from among several for use throughout these experiments, when used with a half-cell consisting of diluted standard acetate buffer (molecular dilution of free acetic acid, 173 l.) prepared from carefully purified acetic acid, gave a potential of 0·5200 volt at 18° and 0·5223 volt at

25°. For the same diluted standard acetate used in conjunction with a decinormal calomel electrode at 18°, Walpole observed 0·6089 volt. It follows that, according to the standards used by Walpole, our electrode A has a potential of 0·2449 volt at 25°, and *that this figure includes the difference of potential at the liquid* junction, since a correction for this is contained in Walpole's data. The *titres* recorded in the *tables* are in c.c. and the *E.M.F.*'s in volts. The remaining data necessary for the application of the Auerbach–Smolczyk equation are recorded in the second, third, and fourth columns of the following table. The calculated values of K_1 and K_2 are in the fifth and sixth columns.

Acid.	Original conc., *M*.	Conc. of NaOH (g. Na/c.c.).	Equivalent titre (c.c.).	$K_1 \times 10^5$.	$K_2 \times 10^6$.
Oxalic	0·05850	0·03671	11·00	—	—
Malonic	0·04991	0·02567	13·42	177	4·37
Succinic	0·04880	0·02567	13·12	7·36	4·50
Glutaric	0·00673	0·002567	18·10	4·60	5·34
Adipic	0·00673	0·002567	18·05	3·90	5·29
Pimelic	0·004835	0·002567	13·00	3·33	4·87
Suberic	0·003295	0·002567	8·86	3·07	4·71
Azelaic	0·0006715	0·0003671	13·00	2·82	4·64

Oxalic Acid.—*E.M.F.* = 0·3341 at titre 0·00 and 0·8590 at titre 11·06.

Titre	0·00	0·51	0·98	1·70	2·41	2·97	3·37	3·79	4·21
p_H ...	1·510	1·560	1·609	1·692	1·787	1·879	1·961	2·056	2·171
Titre	4·62	5·04	5·40	5·80	6·18	6·60	7·00	7·48	8·00
p_H ...	2·315	2·501	2·712	2·970	3·181	3·373	3·536	3·689	3·849
Titre	8·51	8·99	9·49	9·90	10·10	10·29	10·38	10·47	10·52
p_H ...	4·002	4·149	4·331	4·511	4·614	4·736	4·802	4·881	4·927
Titre	10·57	10·61	10·65	10·70	10·75	10·80	10·84	10·89	10·93
p_H ...	5·014	5·025	5·085	5·156	5·239	5·332	5·444	5·610	5·869
Titre	10·97	11·02	11·06						
p_H ...	6·504	9·376	10·390						

These values lie on a smooth curve having two points of inflexion, but, for the reason given on p. 1596, they cannot be represented by an equation of the Auerbach–Smolczyk type.

Malonic Acid.—*E.M.F.* = 0·3668 at titre 0·00 and 0·8466 at titre 13·49.

Titre	0·00	0·50	0·96	1·97	2·98	4·08	5·03	5·72	6·33
p_H ...	2·064	2·158	2·266	2·499	2·719	2·973	3·240	3·494	3·616
Titre	6·74	7·14	7·72	8·50	9·60	10·98	12·00	12·52	12·67
p_H ...	4·090	4·377	4·712	4·957	5·229	5·607	5·925	6·146	6·252
Titre	12·82	12·90	12·98	13·06	13·13	13·20	13·26	13·29	13·33
p_H ...	6·352	6·419	6·507	6·597	6·714	6·858	6·967	7·066	7·245
Titre	13·36	13·39	13·43	13·46	13·49				
p_H ...	7·523	7·951	8·675	9·746	10·180				

Succinic Acid.—*E.M.F.* = 0·3980 at titre 0·00 and 0·8970 at titre 13·48.

Titre	0·00	0·52	1·02	1·56	2·00	2·55	3·54	4·53	5·20
p_H ...	2·591	3·035	3·336	3·617	3·751	3·899	4·120	4·339	4·472
Titre	6·00	6·80	7·63	8·56	10·04	11·52	13·00	13·10	13·20
p_H ...	4·629	4·789	4·947	5·139	5·447	5·837	7·165	8·513	10·364
Titre	13·48								
p_H ...	11·034								

Glutaric Acid.—*E.M.F.* = 0·4365 at titre 0·00 and 0·7930 at titre 18·14.

Titre	0·00	0·30	0·70	1·13	1·59	2·23	2·81	3·40	3·99
p_H ...	3·240	3·340	3·472	3·593	3·709	3·858	3·972	4·074	4·164
Titre	4·62	5·21	5·80	6·49	7·17	7·91	8·70	9·38	10·09
p_H ...	4·257	4·342	4·419	4·505	4·587	4·676	4·768	4·853	4·937
Titre	10·78	11·52	12·21	12·90	13·60	14·30	15·00	15·69	16·44
p_H ...	5·021	5·112	5·202	5·293	5·389	5·499	5·616	5·753	5·946
Titre	16·92	17·27	17·52	17·76	17·91	17·95	18·00	18·05	18·10
p_H ...	6·122	6·297	6·468	6·729	7·000	7·144	7·361	7·749	8·809
Titre	18·14								
p_H ...	9·274								

Adipic Acid.—*E.M.F.* = 0·4390 at titre 0·00 and 0·8030 at titre 18·16.

Titre	0·00	0·21	0·55	0·90	1·26	1·61	1·99	2·45	2·98
p_H ...	3·285	3·372	3·489	3·598	3·700	3·795	3·880	3·976	4·071
Titre	3·62	3·99	4·60	5·18	5·70	6·30	6·89	7·58	8·16
p_H ...	4·175	4·237	4·318	4·399	4·464	4·536	4·602	4·687	4·751
Titre	8·80	9·79	10·64	11·38	12·25	12·98	13·96	15·00	15·56
p_H ...	4·823	4·932	5·029	5·115	5·214	5·309	5·447	5·618	5·726
Titre	16·22	16·76	17·29	17·70	17·89	17·94	17·99	18·03	18·08
p_H ...	5·887	6·066	6·303	6·642	6·963	7·081	7·293	7·579	8·590
Titre	18·12	18·16							
p_H ...	9·105	9·445							

Pimelic Acid.—*E.M.F.* = 0·4464 at titre 0·00 and 0·7910 at titre 13·06.

Titre	0·00	0·31	0·68	1·18	1·69	2·25	2·89	3·42	4·12
p_H ...	3·408	3·536	3·686	3·858	4·016	4·156	4·298	4·404	4·526
Titre	4·81	5·50	6·21	6·93	7·60	8·30	9·02	9·70	10·39
p_H ...	4·628	4·750	4·858	4·963	5·070	5·178	5·301	5·422	5·566
Titre	10·98	11·61	12·15	12·60	12·79	12·92	12·97	13·02	13·06
p_H ...	5·713	5·902	6·146	6·483	6·754	7·208	7·530	8·453	9·240

Suberic Acid.—*E.M.F.* = 0·4519 at titre 0·00 and 0·7805 at titre 8·91.

Titre	0·00	0·30	0·60	0·96	1·49	2·01	2·53	3·00	3·52
p_H ...	3·600	3·763	3·844	4·005	4·192	4·354	4·491	4·609	4·729
Titre	3·99	4·59	5·20	5·78	6·42	7·02	7·60	7·97	8·33
p_H ...	4·837	4·970	5·107	5·240	5·403	5·572	5·785	5·961	6·218
Titre	8·59	8·76	8·81	8·86	8·91				
p_H ...	6·514	6·909	7·248	7·834	9·061				

Azelaic Acid.—E.M.F. = 0·4765 at titre 0·00 and 0·7710 at titre 13·20.

Titre	0·00	0·28	0·58	0·99	1·50	1·96	2·48	3·01	3·50
p_H ...	3·920	3·979	4·030	4·120	4·221	4·307	4·399	4·484	4·567
Titre	3·97	4·50	4·98	5·55	5·98	6·50	7·09	7·52	8·25
p_H ...	4·638	4·721	4·797	4·873	4·941	5·019	5·103	5·174	5·283
Titre	8·90	9·62	10·30	10·83	11·23	11·64	12·00	12·35	12·71
p_H ...	5·394	5·519	5·655	5·782	5·900	6·053	6·206	6·418	6·763
Titre	12·91	13·01	13·10	13·20					
p_H ...	7·225	7·987	8·599	8·903					

THE UNIVERSITY, LEEDS. [*Received, April 11th, 1928.*]

CCVIII.—*The Influence of Arsenic on the Catalytic Activity of Platinum for the Oxidation of Sulphur Dioxide.*

By EDWARD BRADFORD MAXTED and ARTHUR NORMAN DUNSBY.

THE poisoning of a platinum catalyst by means of arsenic is intimately connected with the development of the contact process for the manufacture of sulphuric acid. In spite, however, of the technical and historical importance of this case of inhibition, relatively little has been published on its quantitative aspect; the present work was therefore undertaken with the object of correlating the activity of a progressively poisoned platinum catalyst with its arsenic content.

The kinetics of the reaction between sulphur dioxide and oxygen on the surface of a solid catalyst are complicated (see, for instance, Bodländer and Köppen, *Z. Elektrochem.*, 1903, **9**, 559); but, by working under conditions such that only a small percentage of the possible change takes place, even with an unpoisoned catalyst, the degree of conversion obtained may be regarded as a measure of the activity of the catalyst. For this reason, the measurements were carried out at a relatively low temperature, this being also desirable in order to preclude the possibility of loss of arsenic by volatilisation and in order to eliminate the complication of an equilibrium state appreciably below complete conversion.

The general form of the poisoning curve was found to be similar to that obtained for other reactions (J., 1921, **119**, 225; 1922, **121**, 1760). In the first stages of poisoning, the activity of the catalyst varies approximately linearly with the poison content. This portion of the curve corresponds probably with the saturation by the inhibitant of the regions of special activity which, according to the evidence recently put forward by H. S. Taylor (*J. Physical*

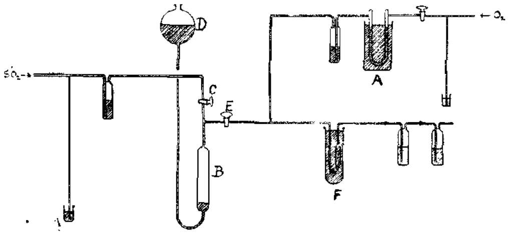
Chem., 1926, **30**, 145; see also Rideal, Deuxième Conseil de Chimie, 1925, Solvay Reports, p. 469) and others, occur on the surface of the catalyst and are apparently responsible for the greater part of its activity. This initial portion of the poisoning curve is followed by a region in which the continued addition of arsenic affects the activity to a far smaller degree.

With the catalyst studied, about 0·0016 g. of arsenic was found to be required to reduce the activity of 1 g. of platinum to one-half of its original value; but this ratio will necessarily be influenced by the degree of subdivision of the platinum.

EXPERIMENTAL.

The apparatus employed is shown diagrammatically in Fig. 1. Electrolytic oxygen, which was passed through the apparatus at

FIG. 1.



a known constant rate, was freed from traces of hydrogen by passage through a tube, *A*, containing platinised asbestos and heated in an oil-bath, following which it was dried by means of sulphuric acid, and allowed to flow, together with sulphur dioxide, over the catalyst. The sulphur dioxide was similarly dried and, by opening the stopcock *C* and closing *E*, a constant volume of the gas was stored in the reservoir *B*, which had a capacity of approximately 80 c.c. This reservoir contained petroleum as the sealing liquid, which was forced into *D* by the pressure of the gas. For each experiment, the constant volume of sulphur dioxide was, by the action of the head of oil in *D*, allowed to flow, together with the oxygen, over the catalyst, the height of *D* being sufficiently above that of *B* to cause an approximately uniform rate of flow throughout the run. In each case, the time of passage of the above volume of sulphur dioxide was 30 minutes, the rate of flow of oxygen being 240 c.c. per hour.

The catalyst tube, which is shown at *F*, had a capacity of about 6 c.c., and contained 0·35 g. of platinum, supported on pumice and prepared by the reduction of platinic chloride with hydrogen. It was heated by immersion in a mercury bath, which contained a thermostat, by means of which the temperature was maintained at 300° with a maximum variation of 2°. The products of the oxidation were passed through two small wash-bottles in series, containing iodine solution, in order to determine—by titration with thiosulphate—the volume of sulphur dioxide which remained unoxidised, the original volume of sulphur dioxide being in each case accurately calculated, by correcting the volume of *B* for the prevailing conditions of temperature and pressure. All parts of the apparatus were sealed together, with the exception of the two wash-bottles which had to be detached for analysis and were connected by ground-in joints.

The solution used for poisoning the platinum contained 0·5 mg. of arsenic per c.c., and was prepared by dissolving the appropriate amount of arsenious oxide in water containing the requisite quantity of sodium hydroxide. After the initial activity of the catalyst had been measured, a known weight of poison was introduced by adding the required volume of the above solution, the water being removed by gentle heating in a current of oxygen. The activity of the partially poisoned catalyst was now determined, following which a further quantity of inhibitant was added, and the measurement of activity repeated, a series of readings being taken at each stage of poisoning. In order to obtain consistent results, it was found necessary, before beginning a test, to allow the sulphur dioxide and oxygen to flow for some time over the catalyst under the conditions subsequently used; and, with this precaution, the method of control and analysis was found to be sufficiently accurate to give reasonably consistent and reproducible results, as is shown by the agreement of the duplicate runs.

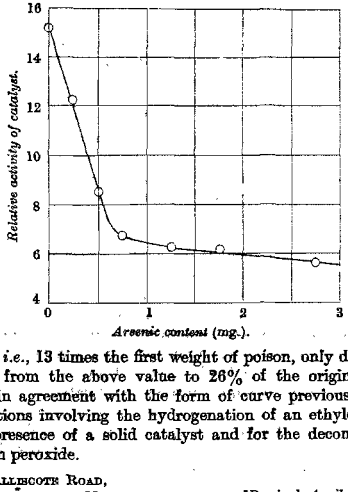
The results of the measurements are in Table I. The average values of the activity at various stages of inhibition have been plotted graphically in Fig. 2 in order to show the form of the

TABLE I.

As content, mg.	G. As per g. Pt.	% of SO_2 oxidised.	Mean.
0	0	15·10, 15·26, 15·12, 15·02, 15·15	15·13
0·25	0·00071	12·12, 12·30, 12·33, 12·22, 11·82, 12·06	12·17
0·5	0·00143	8·56, 8·48, 8·18, 8·90	8·53
0·75	0·00214	6·99, 6·68, 6·65	6·77
1·25	0·00357	6·23, 6·68, 6·05, 6·21, 6·30	6·28
1·75	0·0050	6·08, 6·26, 6·11	6·15
2·75	0·0079	5·65, 5·56	5·60
10·0	0·0286	4·07, 3·99	4·03

poisoning curve. The approximately linear first portion is clearly marked, and after about 0·7 mg. of arsenic, a region of the curve is reached in which the slope towards the activity axis is far less than in the first stages of poisoning; for the first 0·7 mg. of arsenic reduces the activity to 45% of its original value, and a further

FIG. 2.



9·3 mg., *i.e.*, 13 times the first weight of poison, only depresses the activity from the above value to 26% of the original activity. This is in agreement with the form of curve previously obtained for reactions involving the hydrogenation of an ethylenic linkage in the presence of a solid catalyst and for the decomposition of hydrogen peroxide.

38, WALLISCOTE ROAD,
WESTON-SUPER-MARE. [*Received, April 24th*, 1928.]

CCIX.—*On Selenium Tetrafluoride.*

By EDMUND BRYDGES RUDHALL PRIDEAUX and CHARLES BERESFORD COX.

BY passing fluorine over selenium contained in a boat and placed in a copper tube, Lebeau (*Compt. rend.*, 1907, **144**, 1042, 1047) prepared a colourless liquid, which, according to his description, had some properties which differed considerably from those we attribute to selenium tetrafluoride, but which bear certain resemblances to those of the oxyfluoride or of the mixture $SeO_2 + 4HF$ (see table).

The analysis of Lebeau's fluoride corresponded closely to th formula SeF_4, and he was not able to understand why the fluorir ation stopped at this point. It was suggested, however, by Ramsa (*Compt. rend.*, 1907, **144**, 1196) that the presence of copper as reducing agent might have this effect. On another occasio Lebeau (*ibid.*, **145**, 190) succeeded in preparing a gaseous mixture which (when analysed by means of sodium in liquid ammonia) ha a composition approximating to SeF_6 but which contained abou 2% of selenium in excess of the theoretical. The presence of little sodium selenite with the selenide which was formed by treat ment with sodium, suggested to him the presence of a little seleniun oxyfluoride. Although it seems improbable that this would remai after storage over mercury, yet it might very probably have bee formed by the reaction, since fluorine as prepared by Moissan' method is always liable to contain ozone and oxygen. It is als difficult to purify the fluorine completely from hydrogen fluorid carried up from the electrolyte, and this together with the oxy fluoride might well have given a mixture having the correct ratio o selenium to fluorine. The analytical results were expressed as ratio: there is no statement that they were referred to a weighe portion of the liquid, as was done in our analyses.

There is at present, then, some doubt as to the existence of lower fluoride of selenium. The hexafluoride, a stable gas whic did not attack glass, was prepared later in a somewhat impure forn by Lebeau, using the same reaction which had previously given th corrosive liquid. The mode of origin and properties of the latte would therefore seem to require further investigation.

We have now prepared the lower fluoride of selenium by anothe method, *viz.*, the interaction of selenium tetrachloride and silve fluoride. This method excludes the presence of moisture or hydroge fluoride or a higher fluoride of selenium.

EXPERIMENTAL.

The selenium tetrachloride, prepared in the usual manner fron the dry reagents, was kept in sealed sections of glass tube. Th silver fluoride was prepared by the method of Ruff (see this vol p. 739). The fluoride (4—5 parts) and the chloride (1 part) wer mixed in the platinum bottle or the platinum crucible contained i the large monel metal pot. The reaction was started by heatin to 50—60° and then proceeded vigorously. On distillation, colourless, fuming liquid passed over, which was analysed in fraction and gave results corresponding to SeF_4 (J., 1927, 928). As in th case of the oxyfluoride, it was necessary to redistil the product fron silver fluoride in order to remove the chloride completely. Th

yields were low for the reasons already given, but in this case were further reduced by the formation of some oxyfluoride. The analysis of our first product showed a surplus of selenium corresponding to a considerable proportion of this compound. Although it is probably the first product of the hydrolysis of the tetrafluoride, we do not consider that more than a very small amount could have been formed by contact with ordinary moist air, which was, of course, avoided as far as possible. The presence of the oxyfluoride was more probably due to the unavoidable presence in the silver fluoride of silver oxide which could give oxyfluoride, either *via* SeO_2 and SeF_4 or *via* $SeOCl_2$ and 2AgF. On account of this difficulty, the physical properties of the tetrafluoride as given in the table have probably not been defined so well as those of the oxyfluoride. In the next preparation, 9·14 g. of selenium tetrachloride gave 5·12 g. of distillate, the last portions of which appeared slightly milky, perhaps owing to the separation of selenium dioxide. On mixing with the rest of the distillate it became clear. On being redistilled below 140° it yielded 4·42 g. of distillate, *i.e.*, 73·5% of that theoretically obtainable from the tetrachloride taken. This product, analysed by different methods, gave 52·1—51·0% of selenium and 47·2—47·7% of fluorine.

Physical Properties.—The *density* was determined in the monel bottle (this vol., p. 739). It was slightly higher than that of the oxyfluoride and much higher than that of the corresponding mixture of selenium dioxide and hydrogen fluoride.

The *boiling point* was determined in the monel metal bottle. A rapid stream of bubbles began at 91·0° and continued steadily as the temperature was slowly raised to 95°. Heating was continued, until at 124° the bubbles recommenced and continued steadily at that temperature. Since this is the boiling point of selenium oxyfluoride, it is evident that the very small quantity of liquid taken (about 0·4 c.c.) had gained more oxyfluoride by hydrolysis at some stage.

Melting point. The liquid solidified rapidly and completely at −70°. As only 1·476 g. were available for this determination, it was carried out by inspection in a very small platinum crucible which was contained in a glass tube coated inside with a transparent varnish. The pentane thermometer, protected with platinum foil, was inserted so that the bulb was just covered, and the liquid was frozen quickly and allowed to warm slowly. No liquid was seen at −13·0°, whilst all was liquid at −10°. On taking temperature–time readings, a halt was noticed, with oscillations, at −13·0°. The plotted curve showed an inflexion beginning slightly below this point and the melting point from the graph appeared at about

−13·5°. It was therefore much lower than that of the oxyfluoride but much higher than that of Lebeau's preparation.

Chemical Properties.—With silicon (crystalline) an immediate reaction was observed in the cold. This was then carried out in the monel metal boiling-point bottle, which was connected with a nitrometer filled with mercury. The gas collected was silicon tetrafluoride. There was a residue of red selenium in the bottle.

Sulphur gave no reaction in the cold.

Red phosphorus gave a strong reaction with the production of gaseous fluorides, apparently both PF_3 and POF_3, and a residue of red selenium and selenium dioxide. The preparation of selenium fluoride, however, contained some oxyfluoride.

The chemical properties common to selenium tetrafluoride, selenium oxyfluoride, and solutions of selenium dioxide in hydrogen fluoride are:

(1) Strong and complete attack of glass.

(2) Complete hydrolysis by water with evolution of heat and formation of selenious and hydrofluoric acids.

(3) No effect, or only a very slight one, on clean copper.

The chemical properties which show differences are:

(1) The attack on silicon seemed to be directly proportional to the amount of combined fluorine. For a given ratio of fluorine to selenium, it was much greater when the fluorine was present as hydrogen fluoride.

(2) The attack on red phosphorus seems to be proportional to the amount of selenium present in combination or solution, and is inhibited by an excess of hydrogen fluoride.

Properties of the lower fluorides of selenium and of a solution of selenium dioxide in hydrogen fluoride.

	SeF_4 (authors).	SeF_4 (Lebeau).	$SeO_2 + 4HF$.	$SeOF_2$.
Density	2·77	—	2·09	2·67
M. p.	−13·2°	Solid at −80°.	Below about −30° $SeO_2,5HF$ crystallises.	+4·6°
B. p.	+93°	Above 100°.	Indefinite.	+124°
Effect on Si	Strong, giving SiF_4 and Se.	None at b. p.	Strong, giving SiF_4 and Se.	Very slight in cold; on heating, gives SiF_4 and Se.
Effect on S	None in cold.	None at 100°.	Similar to $SeOF_2$.	None in cold; on heating, gives a gas and Se.
Effect on P	Red P. Strong action. Gaseous fluorides, Se and SeO_2. (Sample contained $SeOF_2$.)	White P. Vivid action: gaseous fluorides and Se.	None until excess of HF boils off, then strong.	Very strong in cold: PF_3, POF_3, Se, and SeO_2 formed.

case of the ox still outstanding points in connexion with these com-
silver fluoridch we hope to investigate.

In conclusion, we wish again to acknowledge a grant from the Royal Society to one of us, with the aid of which the indispensable apparatus was acquired.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, April 23rd, 1928.*]

CCX.—*The Laws of Aromatic Substitution. Part VIII.**

By BERNHARD FLÜRSCHEIM and ERIC LEIGHTON HOLMES.

ACCORDING to the theory evolved by one of us, reactivity is governed by three *internal* factors: the *amount* of affinity available at the reacting atom (quantitative factor q); the *nature of this affinity* (polar factor p); and the degree of spatial obstruction (steric factor s). In so far as the problem of substitution in the benzene ring is concerned, the steric effect on positions 3 and 4 exercised by a substituent in position 1 may be neglected. On the other hand, its polar effects on positions 3 and 4 will generally not be the same, but until recently empirical evidence appeared to indicate that the *difference* of the polar effects on the nuclear carbon atoms in positions 3 and 4 was not large enough to produce an appreciable modification of their relative reactivities as determined by the quantitative effect.

On the other hand, Robinson has repeatedly stated that he regards the polar effect (which, according to his theory, would be an electrostatic effect) as one of the chief factors governing aromatic substitution. In Part V (J., 1926, 1562) we have shown that Robinson's view [but not the electrostatic mechanism on which it is based, against which we have adduced arguments (J., 1926, 1566) which have not been refuted] is justified when the quantitative effect is not very pronounced and when, at the same time, the polar effect is at its maximum through proceeding from an actual, undisputed, electrical charge, *viz.*, the charge of an electrolytic ion.† When, however, the polar effect originates in an accumulation

* In Part VII (this vol., p. 453), two important *errata* in the proofs have escaped our attention: On p. 466, section V, first line, "bromomalonic" should read "bromonitromalonic"; and on p. 474, lines 5 to 3 from the bottom, a sentence describing the recovery of *pure* *m*-bromobenzoic acid from nitration 13 has been *transposed*: it should read ". . . 0·160 g. of *m*-bromobenzoic acid (m. p. 143—145°; 152·5—153° on further recrystallisation; mixed m. p.) and 0·045 g. melting at 148—156° (nitrobromo-acids. . . ."

† The first recognition of the effect of electrolytic dissociation on aromatic substitution, and its application to benzoic acid and salts of the benzylammonium series, are to be found in a publication by one of us in *Chem. and Ind.*, 1926, p. 43, issued on Jan. 15th, 1926. Since that date, papers by Soper and Smith and by Ingold and co-workers have been submitted in which the effect of electrolytic dissociation on aromatic substitution (*e.g.*, in phenols) has been further discussed.

of *uncharged* groups of strongly polar nature, our early experiments on the nitration of phenylbromocyanonitromethane appeared to indicate that it can be neglected. Since, however, substitution in this compound, as we now know it to be constituted (see Part VII), is favoured in one and the same position by *both* effects, it appeared desirable to examine the behaviour of substances containing lateral substituents the polar effect of which—if it preponderated—would cause substitution to occur mainly in positions other than those required by the quantitative factor.

Hitherto no examination of the directive effect has been made with a toluene derivative having all its methyl-hydrogen atoms replaced by such "negative" substituents as would, if directly attached to the nucleus, cause preponderating *m*-substitution and which, when attached to the α-carbon atom, should accordingly—if the quantitative (alternating) effect alone were considered—have an *o*-*p*-directive influence. Indeed, no such compounds appear to have been prepared hitherto, with the exception of tribenzoylphenylmethane (Meisenheimer and Weibezahn, *Ber.*, 1921, **54**, 3195)—an unsuitable material owing to the presence of several phenyl groups. We have succeeded in obtaining three such compounds. The preparation and nitration of one of them—*ethyl phenylmethanetricarboxylate* [*ethyl toluene-ααα-tricarboxylate*, $CPh(CO_2Et)_3$]—are described below. For comparison, compounds have also been examined in which some or all of the lateral substituents are groups which in direct attachment to the nucleus would be *o*-*p*-directing. In the present communication we submit quantitative determinations, by our new method (compare Part VI), of the directive effects in the complete series

CH_2PhCl, $CH_2Ph{\cdot}CO_2Et$;

$CHPhCl_2$, $CHPhCl{\cdot}CO_2Et$, $CHPh(CO_2Et)_2$;

$CPhCl_3$, $CPhCl_2{\cdot}CO_2Et$, $CPhCl(CO_2Et)_2$, $CPh(CO_2Et)_3$;

together with two bromo-compounds, CH_2PhBr and $CPhBr(CO_2Et)_2$.

The theoretical conclusions suggested by these experiments will be discussed in detail in Part IX, in conjunction with those indicated by a further series of investigations. Meanwhile it may suffice to summarise the following general points :

1. Our results with ethyl phenylmethanetricarboxylate constitute the first case of preponderating *m*-nitration in the exclusive presence, at the α-carbon atom, of such substituents as would be *m*-directing if directly attached to the nucleus.*

* Phenylnitromethane, which has long been known to be preponderatingly *m*-directing, might be supposed to come under this definition. But in Part X we shall adduce support for its formulation as an equilibrium, $PhCH_2{\cdot}NO_2 \rightleftharpoons$ PhCH—NOH (with O bridging CH and N), in which the bridge form must be regarded as responsible for most of the *m*-nitration.

2. Where the quantitative factor is not very pronounced—*e.g.*, *at an α-carbon which neither forms part of an ethylenic or acetylenic* group nor is linked to substituents possessing a *much* higher or lower affinity demand than hydrogen—and where at the same time the polar factor is very pronounced—*e.g.*, in the case of an α-carbon atom directly linked to an atom charged through electrolytic dissociation, or to several substituents of distinct and similar polarity—there the quantitative factor may be overborne by the polar effect.

3. But even in such extreme cases the quantitative factor can be distinctly traced. For instance, the electrolytic dissociation constants of aromatic acids and bases, substituted in the *m*- or *p*-positions by chlorine on the one hand, by carbethoxyl on the other, show that the polar effect transmitted from these positions is *greater* with carbethoxyl than with chlorine. The *m*-directive effect, however, as evidenced by the results given below, is *less* for carbethoxyl than for chlorine (with the exception of one case where it is equal within the experimental error). Since this quantitative factor—which, as will be shown in Part IX, is much more obvious where the postulated affinity demand is very high and polarity is less pronounced—appears to be capable only of a non-electronic interpretation (at any rate, when it is transmitted through a "single" bond), a non-electronic interpretation appears to be also involved for the polar effect.

4. We interpret * the polar effect as an influence of the *nature* of the chemical affinity of one atom on the *nature* of the chemical affinity of other atoms in the molecule. We regard chemical affinity as the resultant of a distinct chemical attractive force component (one of four different kinds of forces inherent in an atom, the other three being electrostatic, magnetic and gravitational) and an electropolar component. In a free atom both these components will emanate more or less evenly from the whole surface of the atom. Combination of atoms must produce a redistribution of these components along the atomic surface, resulting in an equilibrium; the density of the lines of force of components which attract each other being increased round the point of closest approach between the atoms, the reverse occurring in the case of components which repel each other. Round the point of closest approach, therefore, an increase of density must take place for the lines of force of the chemical component and for electropolar components of opposed sign; for electropolar components of the same sign there must result a decrease of density round the point of closest approach between the atoms, and an increase of density at remote points of

* This should be read in conjunction with Part V (*loc. cit.*), pp. 1563—1564.

the surfaces of the atoms. In this way, the polar component, by a process of inductive transmission (see Flürscheim, *J. pr. Chem.*, 1907, **76**, 189, for comparison with electrostatic induction)—*without the participation of any electrons*—is propagated throughout a chain. This polar effect gradually falls off with the number of intervening atoms (a necessary consequence of the establishment of an equilibrium), and is transmitted from one atom to another (as postulated by one of us in previous papers) to an extent which is a direct function of the affinity content of (*i.e.*, the number of lines of force participating in) the bond between them.

According to our theory of aromatic substitution, this polar effect is, in an overwhelming majority of cases, transmitted to the *p*-position to a greater extent than to the *m*-position. This is due to the *direct* affinity exchange between *p*-atoms postulated by Werner's benzene formula (*Vierteljahrschr. Züricher Naturforsch. Ges.*, 1891, **36**, 1). Only where this residual affinity exchange has been considerably reduced is the reverse to be expected. The exact extent to which such reduction must take place in order to obtain a greater polarity transmission to the *m*-position is an empirical question; present indications suggest that to bring about this result a substituent with a pronounced affinity demand must be present at *each* end of the residual *p*-bond; in such cases (for instance in quinol) the molecule is more or less in a state approximating the quinonoid (compare Flürscheim, *J. pr. Chem.*, 1907, **76**, 203). *At any rate, all compounds of the class examined below* are well within this border line. At all their nuclear carbon atoms, electropolar components of the same sign as those of the lateral substituents are shifted in a direction away from the bonds leading to these substituents, and this shift is greater at the *p*- than at the *m*-carbon atoms. A nitric acid molecule, when approaching these atoms, will find at the accessible (unoccupied) portion of their surfaces more free affinity in the *p*- than in the *m*-position, but in this free affinity the electropolar component—of the same sign as that in the atoms constituting the nitro-group—will predominate more at the *p*- than at the *m*-carbon atom. The result is substitution at *either* atom, in a proportion determined by the relative preponderance of the two conflicting factors.

5. The fact remains, however, that the *existence* of a polar effect on the relative degree of *m*- and *p*-substitution was first postulated by Robinson. For *p*-substitution it had been postulated by one of us long ago.

Table I contains the results calculated from our experiments.

The numbers of the nitrations in Table I correspond to the numbers in Table II. The ratio $m/o + p$ has been adopted as the

TABLE I.*

No.	Compound nitrated.	Medium.	Nitration products (mols. %). Unsubs.	o + p.	m.	Hydrolysis during nitration (% of total halogen).	% Ratio, m/o + p.	Results previously recorded. m, % of total substn.	m/o + p, %.	Authors.
	CH_2PhCl	HNO_3	0 0	88·4 88·4	11·6 11·6	3·2	13·1	—	—	—
	CH_2PhCl	HNO_3 + Ac_2O	3·2	85·2	11·6	0·14	13·6	4·2	4·4	Holleman, *Rec. trav. chim.*, 1914, 33, 1.
	$CH_2Ph{\cdot}CO_2Et$	HNO_3	0	87·9	12·1	0	13·6	9	9·9	Baker and Ingold, J., *1927*, 832.
	$CH_2Ph{\cdot}CO_2Et$	HNO_3	0	88·2	11·8	0				
	$CHPhCl_2$	HNO_3 + Ac_2O	3·2 4·2	63·5 63·0	33·3 32·8	1·0	52·25	33·8	51·05	Holleman, *loc. cit.*
	$CHPhCl{\cdot}CO_2Et$	,,	51·3 55·4	33·9 31·2	14·8 13·4	0·28	43·35	—	—	—
	$CHPh(CO_2Et)_2$	HNO_3	0 0	74·8 74·4	25·2 25·6	0 0	34·05	20	25	Baker and Ingold, *loc. cit.*
	$CPhCl_3$	HNO_3 + Ac_2O	21·6 21·2	30·1 30·2	48·3 48·6	1·35	160·1	64·5	181·7	Holleman, *loc. cit.*
9	$CPhCl_2{\cdot}CO_2Et$	,,	46·9 45·8	20·6 21·1	32·5 32·9	2·15	156·8	—	—	—
10	$CPhCl(CO_2Et)_2$	,,	7·5 6·9	39·5 40·3	53·0 52·8	2·45	132·6	—	—	—
11	$CPh(CO_2Et)_3$	HNO_3	0 0	43·5 43·4	56·5 56·6	0	130·1	—	—	—
12	CH_2PhBr	HNO_3 + Ac_2O	4·7 5·3	88·7 88·1	6·6 6·6	0·38	7·45	—	—	—
13	$CPhBr(CO_2Et)_2$	HNO_3	0 0	60·4 60·8	39·6 39·2	3·2	65·05	—	—	—

* This table was communicated at the meeting of the Society on March 29th (see *Chem. and Ind.*, 1928, p. 369). Subsequently, Ingold and Shaw (this vol., p. 1278, footnote) obtained for benzyl chloride a *m*-proportion of 16%, which differs from our value (11·6%) by far more than the normal error of our method.

standard of comparison because it immediately indicates the relative degree of nitration in these positions, whereas the usual ratio $m/o + p + m$ does not. With the exception of benzal chloride, agreement with earlier results in the five cases where such were available is moderate to poor.

EXPERIMENTAL.

Methods.—(a) *Nitration*. Compounds containing no mobile halogen were nitrated in Kahlbaum's nitric acid, *d* 1·52. For the nitration of compounds containing mobile halogen, a mixture of this acid and acetic anhydride was used (compare Holleman, *Rec. trav. chim.*, 1914, **33**, 1). Benzyl chloride was nitrated both ways (see Nos. 1 and 2), and the results show that these two nitrating media yield values which are identical within the experimental error. Hydrolysed halogen was determined by treating the whole of the diluted and repeatedly extracted spent acid with excess of silver nitrate. The carbethoxy-group remained unaffected during nitration, apart from traces of hydrolysis which were determined by extraction of the products of nitration with bicarbonate. The yields on nitration, allowing for the determined amounts of unnitrated material, varied between 95·5% and 100% of the theoretical. In one case—benzyl chloride in nitric acid alone—the yield was calculated to be 101·8% of the theoretical for complete mononitration. This indication of the presence of a small quantity of dinitro-product was not contradicted by the result of the reduction and bromination of the corresponding acids, since the melting point of the tribromoaniline obtained was slightly low, which it would be if the base were contaminated with a little tribromo-*m*-phenylenediamine.

(b) *Determination of the isomerides*. Oxidation of the products of nitration to the acids was carried out according to the method described in Part V (*loc. cit.*), alkali being, however, added in proportions calculated for each compound so as fully to neutralise any acids produced from its side-chain by oxidation. The acids were then reduced, brominated, etc., as described in Part VI.

Preparation of the Substances used.—(a) *Ethyl phenylmethanetricarboxylate*. 25 G. of ethyl phenylmalonate were added, 2 g. at a time, to 100 c.c. of sodium-dried ether containing 2·5 g. of sodium wire. As much as possible of the ether was then decanted from the sodium salt which had separated, and a further 80 c.c. of dry ether and 15 c.c. of ethyl chloroformate were added with good water-cooling. The sodium salt disappeared and a gelatinous mass took its place. The mass was shaken for 7 hours (although the reaction appeared to be over at the end of 1 hour), and water then

added. The ethereal layer, when dried and evaporated, left a residue which distilled as a colourless, viscous oil, b. p. 154—155°/1·5 mm. (Found : C, 62·3, 62·4; H, 6·6, 6·65. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5%).

(b) *Ethyl phenylchloromalonate.* 10 G. of ethyl phenylmalonate, dissolved in 30 c.c. of carbon tetrachloride, were saturated at 0° with dry chlorine gas and left for 16 hours. After removal of the solvent, the residue was distilled under reduced pressure, giving 2 g. of a fraction, b. p. 70—140°, and 7 g. of the desired *ester* as a colourless, fluid oil, b. p. 143—144°/2—1·5 mm. [Found: Cl (Carius), 13·0. $C_{13}H_{15}O_4Cl$ requires Cl, 13·1%].

(c) *Substances already known.* The remaining compounds used had the following distillation points : benzyl chloride, 177—177·5°; benzyl bromide, 197—198°; benzal chloride, 203—203·5°; benzotrichloride, 213—213·5°; ethyl phenyldichloroacetate, 258—259°; ethyl phenylbromomalonate, 156—157°/2 mm.; ethyl phenylacetate, 226—227°; ethyl phenylchloroacetate, 108—109°/2 mm.; and ethyl phenylmalonate, 151°/8 mm., 140°/3 mm., 135°/1—1·5 mm.

Nitrations.—The conditions and actual weighings in connexion with all the nitrations included in Table I are to be found in Table II. Besides these, nitrations of benzyl bromide and benzal chloride in nitric acid (*d* 1·52) *alone* were carried out, but were found to lead to a very high degree of hydrolysis, with a large increase in *m*-nitration due to the initial formation of benzaldehyde in the latter case and, presumably, of benzyl nitrate in the former. For instance, 10·3 g. of benzyl bromide added within 2 hours to 83 g. of nitric acid (*d* 1·52) and then poured on ice, etc., yielded 12·244 g. plus 0·030 g. of bicarbonate-solnble matter. The spent acid, freed from organic material by repeated extraction with ether, gave with silver nitrate no less than 4·99 g. of silver bromide. 1 G. of the acids obtained by oxidation of the product of nitration yielded 0·007 g. of benzoic acid, 1·390 g. of tribromoaniline, and 0·610 g. of tribromoaminobenzoic acid, corresponding to a ratio $m/p + o$ of 38·6%, compared with the true ratio of 7·45% in the absence of hydrolysis (see Table I).

The standard method of determining the isomerides in the nitration product was only departed from (*a*) in the case of benzotrichloride, where, instead of oxidation, hydrolysis was effected (by Holleman's method) by running 1 part (by weight) of the nitration product into 70 parts (by volume) of boiling 20% hydrochloric acid within 1 hour and boiling for 2 hours; and (*b*) in the case of ethyl phenylmethanetricarboxylate, where, for the first time within our experience with such toluene derivatives, permanganate failed as an oxidant—though even here it had to be resorted to at a later

TABLE II.

No.	Substance nitrated.	G.	Nitrating agent.	Temp.	Duration of addition and standing.	Yield (g.).	$KHCO_3$-soluble (g.).	Oxidised (g.).	Reduction and bromination of acids. Yield of acids (g.).	Found (g.). Reduced (g.).	Benzoic acid.	Tri-bromo-aniline.	Tri-bromo-amino-benzoic acid.	Silver halide from spent acid (g.).	Appearance of nitration product.
1	CH_2PhCl	11·00	88 g. HNO_3	−10° to −8°	2 hrs.; then 15′ at −10°, 15′ at room t.	15·143	+0·053	4·751 2·824	1·730 p- (235—236°) +1·568 0·930 p- (234—235°) +0·849	1·000 0·500	0·008 0·004	1·503 0·740	0·546 0·270	0·401	Semi-solid, pale yellow.
2	CH_2PhCl	12·30	19·5 g. HNO_3 + 10 g. Ac_2O	20—25°	20′; then 15′ at room t.	16·20	—	3·525	1·453 p- (233—235°) +1·590	1·000	0·045	1·429	0·501	0·0188	,,
3	$CH_2Ph{\cdot}CO_2Et$	10·40	83 g. HNO_3	−10° to −8°	90′; then 15′ at −10°, 15′ room.	13·195	+0·056	2·450	1·549	1·000	0·011	1·699	0·265	0	,,
4	$CH_2Ph{\cdot}CO_2Et$	5·61	44 g. HNO_3	−10° to −8°	,,	6·930	+0·033	3·640	1·135 p- (233—236°) +1·029	1·029	0·005	1·492	0·566	0	,,
5	$CHPhCl_2$	10·14	in 10 c.c. Ac_2O; this added to 20 g. HNO_3 + 10 g. Ac_2O	15—18°	20′; then 10′ room.	12·40	—	2·859 4·522	1·921 1·050 p- (233—236°) +1·759	1·000 1·000	0·023 0·050	1·263 0·833	0·752 1·188	0·1811	Oil, pale yellow.
6	$CHPhCl{\cdot}CO_2Et$	6·253	8·4 g. HNO_3 + 4·2 g. Ac_2O	15—16°	25′; then 15′ room.	8·800	—	5·100 2·600	2·607 1·332	1·000 1·000	0·428 0·469	0·765 0·716	0·380 0·350	0·0168	Oil, very slightly yellow.
7	$CHPh(CO_2Et)_2$	10·88	88 g. HNO_3	−10° to −8°	1 hr.; then 30′ at −10°, 15′ room.	12·801	+0·070	1·901 4·044	0·905 1·800	0·500 1·000	0·006 0·009	0·708 1·426	0·271 0·555	0	Oil, brown.
8	$CPhCl_3$	10·63	in 10·5 c.c. Ac_2O; this added to 16 g. HNO_3 + 8 g. Ac_2O	17—19°	15′; then 12½′ room.	12·666	—	2·080 2·141	hydrolysed all ,,	 ,,	0·237 0·241	0·892 0·928	1·620 1·692	0·3160	Oil, pale yellow.
9	$CPhCl_2{\cdot}CO_2Et$	5·39	4·5 g. HNO_3 + 2·25 g. Ac_2O	20°	20′; then 15′ room.	5·92	—	2·724 2·865	1·280 1·299	1·000 1·000	0·384 0·361	0·456 0·450	0·815 0·796	0·1429	,,
10	$CPhCl(CO_2Et)_2$	6·95	5·2 g. HNO_3 + 2·6 g. Ac_2O	20°	10′; then 40′ room.	7·97	—	2·188 2·440	0·864 0·972	0·800 0·800	0·042 0·039	0·601 0·619	0·927 0·920	0·0904	,,
11	$CPh(CO_2Et)_3$	6·90	55 g. HNO_3	−10° to −9°	20′; then 5′ at −10°, 60′ at room.	7·812	+0·040	2·545 3·340						0	,,
12	CH_2PhBr	10·11	in 20 c.c. Ac_2O; this added to 11·9 g. HNO_3 + 5·6 g. Ac_2O	16—16°	45′; then 10′ room.	12·53	+0·028	2·28 2·77	1·394 1·760	1·000 1·000	0·084 0·039	1·745 1·760	0·148 0·150	0·0425	Sticky solid, yellow.
13	$CPhBr(CO_2Et)_2$	11·10	90 g. HNO_3	−10°	1 hr.; then 30′ at 10°, 15′ room.	12·555	+0·045	4·800 3·44	1·721 1·185	1·000 1·000	0·011 0·015	1·185 1·190	0·882 0·868	0·210	Oil, pale yellow.

stage of the oxidation process. No doubt owing to steric hindrance (compare the well-known resistance of the analogously constituted esters of triphenylacetic acid to hydrolysis), the side chain was attacked so slowly by the permanganate that in the meantime the greater part of the product was destroyed by nuclear oxidation. Attempts to hydrolyse the ester to the acid (and thereby obtain nitrophenylacetic acid) also failed; but initial boiling with dilute nitric acid of Baker and Ingold's concentration, followed by treatment with permanganate as indicated by us, achieved the desired result.

Our usual method of permanganate oxidation gave 30 mol. % of acids, or less. Hydrolysis by 10 parts (by vol.) of sulphuric acid (d 1·19) and 4 parts (by vol.) of alcohol per part of ester gave, even when carried out for 40 hours at 130°, on subsequent oxidation with permanganate, only 0·355 g. of acids from 2·45 g. of the ester. Hydrolysis by boiling with 5% aqueous sodium hydroxide appeared to produce nitrophenols.

Action of Dilute Nitric Acid on Nitrated Ethyl Phenylmethanetricarboxylate, followed by Treatment with Permanganate.—2·545 G. of the nitrated oil were boiled for 12 hours with 40 c.c. of nitric acid (d 1·125). The acids formed were then separated from the unaltered ester, and the latter was boiled for 12 hours with 30 c.c. of the above nitric acid. 0·190 G. of the ester was still unchanged. This was boiled for 27 hours with 10 c.c. of the nitric acid and yielded 0·030 g. of acids and 0·115 g. of ester. This 0·115 g. was oxidised for another 27 hours with nitric acid, then with a little permanganate, and yielded 0·024 g. of acids, m. p. 115—125°, giving on reduction, etc., 0·036 g. of tribromoaniline together with a mere trace of tribromoaminobenzoic acid. Similarly, the above 0·030 g. of acids, when boiled with permanganate (0·03 g.) for 1 hour, and reduced, etc., gave 0·033 g. of tribromoaniline and a mere trace of the amino-acid. The main fraction of the acids (1·305 g.), as indicated by its yield, was of higher molecular weight than nitrobenzoic acid, but gave the latter, by 1 hour's boiling with 1·5 g. of permanganate, in a yield of 0·821 g., from which, on reduction, etc., 0·617 g. of tribromoaniline and 1·103 g. of tribromoaminobenzoic acid were obtained. In a repetition of the oxidation 3·34 g. of the original nitrated oil were boiled with 40 c.c. of the nitric acid for 9 hours, and the acid and ester fractions were separated. The ester fraction was again boiled with nitric acid for 9 hours and separated, and so on, such boiling being altogether performed four times. The residual ester fraction then weighed 0·301 g. The united (incompletely oxidised) acid fractions were boiled with 2 g. of permanganate for ½ hour, and the nitrobenzoic acids (1·019 g.)

obtained were reduced, etc., yielding 0·745 g. of tribromoaniline and 1·400 g. of tribromoaminobenzoic acid. Since in this repetition the acids produced were exposed for a shorter time to subsequent destructive oxidation than in the first experiment, and since the relative yields of *m*- and *o*-,*p*-acids were identical in both experiments, the figures obtained may be regarded as conclusive notwithstanding the prolonged oxidation. It is seen that the final, most resistant, ester fraction contained scarcely any *m*-isomeride. It might be expected that the *o*-isomeride would be most difficult to oxidise in such a case, and the melting point of the nitrobenzoic acid (see above) obtained from the residual ester of the first experiment confirms this by indicating the absence also of the *p*-isomeride. The 0·301 g. of residual ester obtained in the repetition melted at 78—80°, and, after recrystallisation from petrol (b. p. 60—80°), 0·248 g. of colourless prisms was obtained, showing the constant m. p. 83—84° (Found: N, 4·3. $C_{16}H_{19}O_8N$ requires N, 4·0%). The compound is, therefore, *ethyl o-nitrophenylmethanetricarboxylate*.

We desire to record our indebtedness to the Advisory Council of the Department of Scientific and Industrial Research, and to the Government Grant Committee of the Royal Society, for grants to one of us (E. L. H.); also to Sir W. H. Bragg and the Royal Institution, who have placed at our disposal the facilities of the Davy Faraday Laboratory, where the work was carried out.

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CCXI.—*The Action of Phosphorus Pentachloride on Homophthalic Acid.*

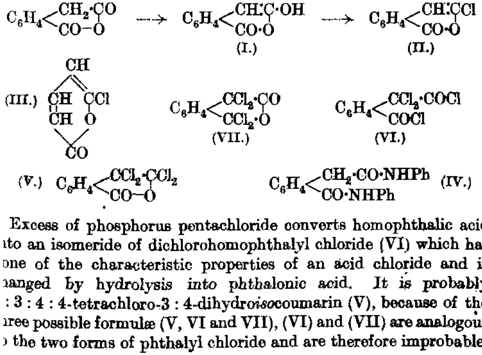
By WILLIAM DAVIES and HARRY GORDON POOLE.

WITH a view to study the relationship of the three possible forms of homophthalyl chloride, the reaction of phosphorus pentachloride with homophthalic acid has been investigated: instead of homophthalyl chloride, however, 3-*chloroisocoumarin* (II) and 3 : 3 : 4 : 4-*tetrachloro*-3 : 4-*dihydroisocoumarin* (V) were formed. Neither phosphorus pentachloride nor thionyl chloride seems capable of converting homophthalic acid or its anhydride into homophthalyl chloride, which is still unknown.

The explanation of the production of (II) is to be found in the existence of homophthalic anhydride in the enolic form (I). Dieckmann (*Ber.*, 1914, **47**, 1428) has shown that some of the reactions of homophthalic anhydride, and the production of a yellow colour

uring hydrolysis (*ibid.*, p. 1435), can be explained by means of this ›rmula, and a proof of the existence of (I) in solution is now given. he existence of (I) and its conversion into (II) show the great ›semblance of homophthalic to glutaconic anhydride, which can e converted into its chlorine derivative (III) (Bland and Thorpe, ., 1912, **101**, 864).

The constitution of 3-chloro*iso*coumarin is shown by its conversion ıto homophthalic acid by alkaline hydrolysis, and also by its con- ersion into a compound which is not homophthalanil (Dieckmann, *c. cit.*, p. 1434), and is probably *homophthalanilide* (IV). 3-Chloro- *o*coumarin is much less reactive towards non-alkaline solutions ıan a true acid chloride and it distils in steam almost unchanged. he formula (II) does not, however, represent some of its properties, ır despite its " unsaturated " character it is stable towards some on-alkaline oxidising and reducing agents and is not attacked by romine in benzene. In some respects the lack of activity shows ıat the double bond is of " aromatic " character.



Excess of phosphorus pentachloride converts homophthalic acid ıto an isomeride of dichlorohomophthalyl chloride (VI) which has one of the characteristic properties of an acid chloride and is ıanged by hydrolysis into phthalonic acid. It is probably : 3 : 4 : 4-tetrachloro-3 : 4-dihydro*iso*coumarin (V), because of the ıree possible formulæ (V, VI and VII), (VI) and (VII) are analogous › the two forms of phthalyl chloride and are therefore improbable.

EXPERIMENTAL.

Homophthalic Acid.—The best method of preparing homophthalic cid is by the reduction of phthalonic acid after the method of Graebe nd Trumpy (*Ber.*, 1898, **31**, 375; Dieckmann and Meiser, *Ber.*, 908, **41**, 3258, Anm. 1), now that this acid is easily accessible (von ›raun, *Ber.*, 1923, **56**, 2333). The following conditions give phthalonic cid, containing less than 0·5% of phthalic acid, in yields up to 82%

calculated on the permanganate used. Tetrahydronaphthalene (250 g.) is vigorously stirred in 12 l. of gently boiling water while powdered potassium permanganate (2000 g.) is introduced in 5 to 10 g. lots during about 8 hours; tetrahydronaphthalene vapour is apt to escape, and the process is finished when the permanganate no longer causes a vigorous reaction. Von Braun does not state the proportion of water to the permanganate or tetrahydronaphthalene used, and our experience is that a small quantity of water makes the reaction difficult to control and notably increases the quantity of phthalic acid produced. This important point has also escaped Cornellot (*Ann. Chim.*, 1927, 7, 281), and the presence of our relatively very large proportion of water renders Cornellot's delicate temperature control unnecessary, provided that the apparatus has a thoroughly efficient condenser such as of the Munich worm type. The phthalonic acid is worked up after von Braun, and our yields are intermediate between his and those of Cornellot. The conversion into homophthalic acid has been carried out almost quantitatively on a large scale; if the phthalonic acid is moist, or the hydriodic acid weaker than the constant-boiling mixture with water, a small quantity of phthalidecarboxylic acid (m. p. 152°, identified by the method of mixed melting points) is produced. This is separated from homophthalic acid by means of its greater solubility in water. The homophthalic acid so produced melts at 181°, and its anhydride at 141—142°.

Proof of the Existence of the Enolic Form of Homophthalic Anhydride (I).—Dieckmann (*loc. cit.*, p. 1429) states that homophthalic anhydride shows no distinct reaction with ferric chloride, but this can be obtained as follows: A dilute alcoholic solution of homophthalic anhydride is treated with $N/10$-potassium hydroxide, the cold yellow solution made faintly acid with dilute sulphuric acid, and a drop of ferric chloride solution immediately added. A bluish-violet coloration is produced which lasts a considerable time. If many minutes are allowed to elapse between the addition of the sulphuric acid and of the ferric chloride, the coloration is very faint or non-existent.

3-*Chloroisocoumarin* (II).—A tarry mass is produced when homophthalic anhydride is heated with phosphorus pentachloride and a small quantity of phosphorus oxychloride, but when homophthalic acid (20 g. = 1 mol.) is heated with phosphorus pentachloride (50 g.: 10% excess of 2 mols.) and phosphorus oxychloride as solvent (50 g.) for 3 hours at 140—150°, a smooth reaction ensues. The phosphorus oxychloride is removed by distillation in a vacuum, water added, and the 3-*chloroisocoumarin* distilled in steam. The product (about 5 g.) is readily obtained almost pure (m. p. 95°) by crystallisation

from light petroleum, but is obtained quite pure by crystallisation from ethyl ether. 3-*Chloroisocoumarin* forms lachrymatory white needles, m. p. 98·5—99°, b. p. about 150°/5 mm., and is very soluble in ether, benzene and alcohol, moderately easily soluble in light petroleum, sparingly soluble in hot and practically insoluble in cold water, from which it can be crystallised. The solutions of the pure substance in organic solvents have a strong blue fluorescence (Found: C, 59·5; H, 2·6; Cl, 19·5; *M* in benzene, 177; by Rast's method, 207. $C_9H_5O_2Cl$ requires C, 59·8; H, 2·8; Cl, 19·7%; *M*, 180·5). When it is boiled with a solution of excess of aniline in benzene, and the mixture kept for 48 hours, *homophthalanilide* (IV) is slowly precipitated; this crystallises from alcohol in very long, thin needles, m. p. 231·5°, which become electrified when shaken in a glass bottle or stirred with a glass rod (Found: N, 8·3, 8·5. $C_{21}H_{18}O_2N_2$ requires N, 8·5%).

3-Chloro*iso*coumarin is remarkably stable towards neutral or acid hydrolytic agents, no hydrogen chloride being obtained by boiling its aqueous or alcoholic solutions for a short time. It is also stable to prolonged treatment with boiling formic acid, sodium iodide in boiling acetone solution, hydriodic acid, and zinc with acetic acid. The chlorine atom is more labile in alkaline media. 3-Chloro*iso*-coumarin in dry benzene reacts very slowly with dry ammonia, but when a trace of moisture is introduced by exposure to the atmosphere the reaction mixture rapidly becomes yellow, brownish-green, and finally bluish-green. From the green precipitate by solution in benzene a small quantity of colourless needles, m. p. 126°, is isolated. This substance is almost certainly *o*-carboxyphenylacetonitrile (see Haworth and Pink, J., 1925, **127**, 1370).

3-Chloro*iso*coumarin reacts readily with aqueous sodium hydroxide to form a yellow solution, and the ultimate product is homophthalic acid (this and the anhydride from it were identified by the method of mixed melting points). The yellow solution reduces permanganate to manganate instantly, but when it is boiled or acidified it loses its colour and reducing properties. 3-Chloro*iso*coumarin itself does not reduce potassium permanganate in neutral acetone solution. The qualitative behaviour of homophthalic anhydride in sodium hydroxide solution towards heat and towards potassium permanganate is the same as that of 3-chloro*iso*coumarin, the view that the chlorine atom is replaced by the —ONa group thus being confirmed.

3 : 3 : 4 : 4-*Tetrachloro*-3 : 4-*dihydroisocoumarin* (V).—Homophthalic acid (54 g.), mixed with phosphorus pentachloride (250 g. : 4 mols.) and phosphorus oxychloride (100 g.), was heated for 8 hours at 140—150° and the phosphorus oxychloride and the residue were

then distilled in a vacuum. The main fraction (40 g.), b. p. 170—190°/21 mm., solidified on cooling. A further quantity of crystals was obtained by the addition of light petroleum (b. p. 80—100°), and crystallisation from this solvent gave pure 3 : 3 : 4 : 4-*tetrachloro*-3 : 4-*dihydroisocoumarin* (12 g.) in white, compact crystals, m. p. 122° (Found : C, 38·2; H, 1·8; Cl, 49·5; *M*, by Rast's method, 266. $C_9H_4O_2Cl_4$ requires C, 37·8; H, 1·4; Cl, 49·6%; *M*, 286). It slowly reacts with excess of aniline in hot benzene to produce a chlorine-free *anilide*, m. p. 225°, which is quite distinct from the anilide previously described, m. p. 231·5°.

The dihydro*iso*coumarin, which is further attacked by phosphorus pentachloride at high temperatures to give an oily mixture, resembles 3-chloro*iso*coumarin in the general inertness of the chlorine atoms, and in this case even the hydrolysis in boiling aqueous-alcoholic sodium hydroxide solution is extremely slow. The product of hydrolysis is phthalonic acid. This was identified by conversion into a *compound* (cream-coloured, felted needles, m. p. 239°) with *p*-nitrophenylhydrazine which was also obtained from an authentic specimen of phthalonic acid.

THE UNIVERSITY OF MELBOURNE. [*Received, March* 19*th*, 1928.]

CCXII.—*On Active Nitrogen. Part V. The Decay of the Nitrogen After-glow.*

By ERIC JOHN BAXTER WILLEY.

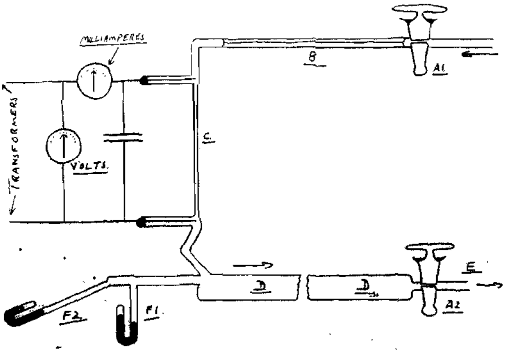
IN searching for information which would reconcile the evidence as to the energy and nature of active nitrogen, as presented in the present series of papers, with the results obtained by spectroscopists, it appeared that a study of the decay process of the glow would probably be of considerable value. Lord Rayleigh has shown (*Proc. Roy. Soc.*, 1912, *A*, **86**, 262; **87**, 179) that the glow transformation is multimolecular, whereas the results of Angerer (*Physikal. Z.*, 1921, **22**, 97) and of Bonhoeffer and Kaminsky (*Z. physikal. Chem.*, 1927, **127**, 385) indicate that it is bimolecular with regard to the active nitrogen. The assumption of a simple process of recombination of nitrogen atoms, as postulated by Angerer and to a certain extent by Bonhoeffer and Kaminsky and others in explanation of this result, is open to certain formidable objections, *viz.*, (*a*) the negative temperature coefficient of the glow decay (Rayleigh, *loc. cit.*), and (*b*) the familiar and marked destructive effect of the surrounding gas on the glowing nitrogen, first observed by Rayleigh (*Proc. Roy. Soc.*, 1916, **92**, 438).

In Part I (J., 1926, 1804) it was suggested that there are some points of similarity between the nitrogen glow-decay process and the reaction $2NO + O_2 \longrightarrow 2NO_2$, which has been shown by Bodenstein and Lindner (*Z. physikal. Chem.*, 1922, **100**, 68) to be kinetically of the third order and to possess a true negative temperature coefficient. If this hypothesis be correct, the total pressure of the nitrogen will exert a great influence on the decay process of the glow, and the present communication describes an investigation of the matter.

EXPERIMENTAL.

Nitrogen purified as before (Part I, J., 1926, 1804) was drawn *via* the tap A1, through the capillary choke B, the discharge tube C,

FIG. 1.



the observation tube D, and the tap A2 to exhaust at E (see Fig. 1). Two manometers, one vertical (F1) and the other inclined (F2), were provided, and a cadmium trap for mercury vapour (omitted from the diagram) was interposed between the manometers and the gas line; this last arrangement was deemed advisable since the quantity of mercury vapour gaining access to the discharge even at ordinary temperatures is sufficient to produce a noticeable fouling of the apparatus after continuous running for a week or two. Aluminium electrodes were used as before. The discharge was obtained from the 100-cycle converter and transformers mentioned in the previous paper, and could, if desired, take 300 milliamps. at 10,000 volts on full load ; this was greatly in excess of normal requirements

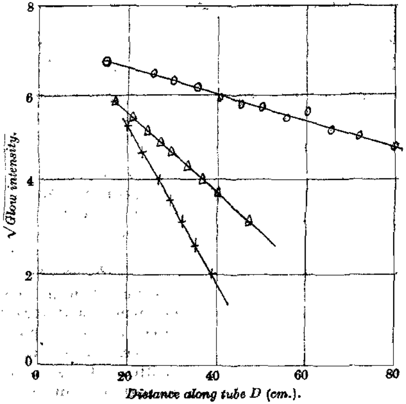
and an r.m.s. current of 20 milliamps. was generally used, four quart-size Leyden jars being provided in parallel with the discharge as shown. A brilliant glow was obtained when the gas was drawn through the apparatus at flow speeds up to 3500 c.c./hr. (at *N.T.P.*) and pressures of 10 mm. and less. Before being fitted, the discharge and observation tubes were cleansed as already described (Part I) and the electrodes submitted to a long preliminary run in another tube to free them thoroughly from gas. D was about $1\frac{1}{2}$ m. long and of 2 cm. internal diameter, and all glass parts were heated as strongly as possible under a pressure of 0·0001 mm. before starting the experiments.

The intensities of the glow were measured by means of an Eastman colorimeter (*Nature*, 1926, **118**, 30; see also Jones, *J. Opt. Soc. Amer.*, 1920, **4**, 420). The observation field of this instrument is divided into upper and lower halves, one giving direct vision of the substance to be examined, and the other being illuminated by a small constant-current glow lamp, the light from which passes through four wedges of gelatin dyed respectively red, green, blue, and " neutral " or grey. These wedges can be introduced to any degree desired, either singly or in combination, according to an arbitrary scale which reads from 0 to 50 for each. Since the colour-quality of the glow does not appreciably alter during decay, the process can conveniently be followed by matching the initial intensity by means of the red, green, and blue wedges and introducing the grey as the luminosity decreases with the passage of the gas along D. The instrument was mounted so as to be movable parallel to the observation tube and at a fixed distance, its position being read by means of a pointer on the base which moved along a scale placed below the tube containing the glowing gas. The intense light from the discharge was screened off by means of black cloth, and a similar black background was provided for the observation tube.

In the experiment, the glowing nitrogen was first drawn through the apparatus for some 20—30 minutes in order that the intensity, often low at first, should rise to its constant value. The comparison and observation fields were then matched, the " neutral " wedge remaining at zero, the colorimeter was moved along D, and the intensities were re-matched at about ten fixed points by means of the " neutral " wedge. Since the reading on this is 50 when fully introduced, the intensity of the glow on the arbitrary scale of the instrument is (50 minus the scale reading of the wedge). This procedure was repeated on the return journey of the colorimeter to its zero position, the points at which the observations were made in this case being half-way between those for the outward journey. Measure-

ments of the decay of the glow along D were thus obtained under a variety of conditions of flow speed and pressure, these being determined respectively by a calibrated Venturi meter in the gas line and by the tilted manometer F2, the vertical gauge serving to check the former. Curves were then plotted showing the relation between *the square root of the intensity and the time, the latter expressed* in terms of the distance along the scale below the observation tube. Typical results are shown in Fig. 2.

Fig. 2.



⊙ = 3·5 *mm.* 1150 *c.c./hr.* △ = 5·0 *mm.* 1150 *c.c./hr.*
+ = 7·0 *mm.* 2200 *c.c./hr.*
(*Flow speeds given at atmospheric pressure.*)

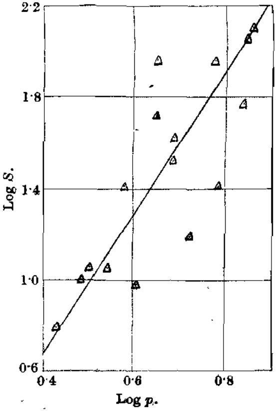
In order to reduce these observations to a common basis for comparison, the following procedure was adopted. Applying Boyle's law, we see that if distances along the observation tube are to be taken as expressing times the slopes of the lines as actually observed must be multiplied by the gas pressure and divided by the flow rate in order that comparable results shall be obtained; it is unnecessary to express them upon an absolute basis. The "corrected" slopes × 100 are in Table I, and it will be noticed that the greater the pressure the greater the gradient, *i.e.*, the rate of decay increases with the gas pressure: moreover, when the logarithms of

TABLE I.

No.	Expt.	Observed slope.	Pressure (mm.).	Flow rate (c.c./hr.).	Corrected slope, S.	log p.	log S.
A.	1	0·051	4·0	2200	9	0·60	0·97
	2	0·178	7·0	,,	57	0·84	1·76
	3	0·062	5·3	,,	15	0·72	1·17
	4	0·086	6·2	,,	24	0·79	1·38
B.	1	0·036	3·5	1150	11	0·54	1·04
	2	0·094	5·0	,,	41	0·69	1·61
	3	0·188	7·3	,,	120	0·86	2·08
	4	0·039	3·2	,,	11	0·50	1·04
	5	0·180	7·0	,,	110	0·84	2·04
	6	0·076	5·0	,,	33	0·69	1·52
C.	1	0·03	2·7	1320	6	0·43	0·78
	2	0·15	4·5	,,	51	0·65	1·71
	3	0·03	3·0	900	10	0·48	1·00
	4	0·06	3·8	,,	26	0·58	1·40
	5	0·17	4·5	,,	87	0·65	1·94
	6	0·136	6·0	,,	90	0·78	1·95

the slope S and the gas pressure p are plotted against each other, v *find that the slope of the line thus obtained gives fairly close* $\log S/\log p = 3$, *i.e.*, *the slo varies as the cube of the g pressure* (Fig. 3).

FIG. 3.



Experiments A3, A4, a C5 are doubtful but ha been included for complet ness.

Discussion.

Let us follow the consens of opinion and regard t after-glow as representi the energy of recombinati emitted either as a whole *in part as radiation cons* quent upon binary collisio among atoms. The glo intensity I expressed on arbitrary scale will then proportional to the rate which the atoms are recon bining, and if ν be th concentration at any instar $d\nu/dt = kI$, where k is a co stant. If Z be the number of such collisions per second, we have

$$Z = \nu^2[2\sigma^2\sqrt{4\pi BT/m}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where σ = diameter of nitrogen atom, taken as $1·9 \times 10^{-8}$ cm m = mass of nitrogen atom, taken as $2·3 \times 10^{-23}$ g.; B = Bolt

ıann's constant $= 1{\cdot}37 \times 10^{-16}$; and $T =$ absolute temperature, ıken as 288°. Hence K (the quantity in the square bracket) $=$ ·05 × 10^{-10}, and

$$d\nu/dt = kI = K\nu^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

hence it follows that if a linear relation exists (such as these experiıents show) between $\sqrt{I}$ and t, the decay process is bimolecular ith respect to the glow-producing system. This is in complete greement with the conclusions of other investigators (*vide supra*), ıd hence we may write $d[N]/dt = K[N]^2$. The slope of the $\sqrt{I}$–t curve should not, however, be affected in any way by the total ıs pressure, as in these experiments, but be determined solely by ıe constant K; we are thus led at once to the conclusion that the ecay process is not kinetically a binary reaction except with respect ı the glow-producing system, assumed atomic. We may examine ıe hypothesis of a ternary reaction as follows.

By equation (2) we have $d\nu/dt = K\nu^2$, and integration of this from ı initial concentration of atoms α when $t = 0$ to a value ν at time gives

$$Kt = \int_{\nu}^{\alpha} d\nu/\nu^2 \text{ or } K = (\alpha - \nu)/t\alpha\nu \quad . \quad . \quad . \quad (3)$$

his is the usual equation for the velocity coefficient in a bimolecular action. Bodenstein and Lindner (*loc. cit.*) have shown that ood agreement between calculated and observed values for elocity coefficients in the reaction $2NO + O_2 \longrightarrow 2NO_2$ may be otained upon the assumption that the probability of an oxygen olecule striking a nitric oxide molecule actually in collision with ıother bears to the probability of the binary collision the same lation as the molecular diameter does to the mean free path (see inshelwood, "Kinetics of Chemical Change in Gaseous Systems," 111); applying this reasoning to the hypothetical reaction $N + N_2 \longrightarrow 2N_2$, we have, for nitrogen at 10 mm. pressure, $8 \times 10^{-8} \div 4{\cdot}5 \times 10^{-4} = 8{\cdot}4 \times 10^{-5}$ as the ratio of ternary to nary collisions, *i.e.*, as the ratio of the rates of the reactions $N + N_2 \longrightarrow 2N_2$ and $N + N \longrightarrow N_2$. We may then transform ıuation (3) to one for calculations in ternary collisions by multiplyg the velocity coefficient K by this quantity. Taking 3 secs. as e average visible life of the glow in nitrogen at 10 mm. pressure, ıd assuming that it corresponds to a change of intensity from to $I/100$, *i.e.*, to a change of concentration of atoms from α to ν, here $\nu = \alpha/10$, we have (from equation 3)

$$K \times 8{\cdot}4 \times 10^{-5} = \frac{1}{3}\left(\alpha - \frac{\alpha}{10}\right)\frac{10}{\alpha^2},$$

ıd since $K = 1{\cdot}05 \times 10^{-10}$, $\alpha = 3{\cdot}4 \times 10^{14}$ atoms per c.c. Since

3 H

the concentration of chemically active nitrogen (1—1·5%) is approximately 4×10^{15} molecules per c.c., it follows that the assumption of a ternary process renders it just possible for the glowing and chemically active forms of nitrogen to be identical, or, more probably (see later), present in comparable concentrations, provided (*a*) that an extremely high fraction of the total atomic collisions (*i.e.*, N + N impacts) results in the production of a complex which can within its life, since it is likely to be "excited," undergo collision with another neutral molecule, and (*b*) that we are justified in assuming the same molecular diameter to obtain in the neutral and excited states. We may assume that condition (*a*) is likely to be realised (see Hinshelwood, *op. cit.*, p. 101), but with regard to (*b*), Stuart (*Z. Physik*, 1925, **32**, 262), Tolman, Yost, and Dickinson (*Proc. Nat. Acad. Sci.*, 1927, **13**, 188), and others have shown that the diameter of an excited or "active" molecule may be considerably greater than the normal; were this so in the present case an increase in σ would diminish the values calculated for the concentration of chemically active nitrogen. It is also clear that the assumption of a purely binary decay will lead to a concentration of glowing nitrogen of the order 10^{-5}—10^{-6} of the chemically active nitrogen. It appears then that by this simple calculation we can obtain excellent correlation between the life of the glow and the quantity of chemically active nitrogen present, but if the glow decay were truly ternary, its rate would vary inversely as the mean free path of the nitrogen molecule, *i.e.*, as the total pressure p, and not as p^3.

The author suggests that this difficulty is overcome by the hypothesis that the decay process really consists of an initial ternary collision $2N + N_2 \longrightarrow 2N_2$ followed by two binary impacts, one of the two entities concerned in each of these last two being neutral nitrogen molecules.

Consequences of this hypothesis are as follows:

(*a*) The decay process is binary with respect to the atoms but effectively ternary, since the last two binary reactions will be much more rapid than the relatively slow ternary reaction which determines the effective speed of the glow transformation and accounts for the comparable values calculated and observed for the concentration of chemically active nitrogen. The total reaction will, however, be of the fifth order since we have

$$d[N]/dt = \text{constant} \times [N]^2 \quad . \quad . \quad . \quad . \quad (4)$$

and as the slope of the $\sqrt{I}$–t curve, *i.e.*, the value of the constant, varies as p^3, we have finally

$$d[N]/dt = K_2[N]^2[N_2]^3 \quad . \quad . \quad . \quad . \quad (5)$$

(*b*) The negative temperature coefficient of the glow decay is

accounted for, since this is probably a characteristic feature of ternary reactions (see Hinshelwood, *op. cit.*, p. 111).

(*c*) The decay process is to be regarded as a series of (possibly) complicated reactions, and if we accept the possibility of externally induced changes in the mechanism, the independence of glow and chemical activity (J., 1927, 2831)—see also Kenty and Turner (*Physical Rev.*, 1927, **29**, 914)—is rendered probable under appropriate conditions. The author now prefers this hypothesis to that advanced in the earlier communication (Part IV), *viz.*, that the glowing and chemically active forms of nitrogen, while generally co-existent, are nevertheless not interdependent.

(*d*) The volume change attendant upon the production of the atoms need not be more than quite a small fraction of the volume of chemically active nitrogen, since it follows naturally that the latter may represent *metastable or isomeric nitrogen molecules* produced during the decay and each possessing a part of the energy of the parent body. This would explain Crew and Hulbert's observation (*Physical Rev.*, 1927, **30**, 134) that no appreciable increase in pressure due to dissociation occurs when a discharge is passed in nitrogen under such conditions as to develop the glow. The decay process might thus tentatively be envisaged

$$2N + N_2 \longrightarrow N_2^A + N_2^B \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$
$$N_2^A + N_2 \longrightarrow N_2^C + N_2^D \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$
$$N_2^B + N_2 \longrightarrow N_2^E + N_2^F \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where N_2^A, etc., represent the various molecules which have acquired fractions of the original energy of recombination. This may not represent the *whole* of the decay process since it simply describes what can be *seen*—the possibility of other "dark" reactions after this must be kept in mind, particularly as after the emission of the α- or visible radiation the molecule is still 8·0 volts above the normal electron level (Johnson, *Nature*, 1927, **119**, 9). In this way we see that comparable values should be obtained for the active nitrogen concentrations as measured chemically and as calculated from the life of the glow, a ternary decay being assumed.

(*e*) If we accept the very probable view that one at least of these decay stages results in the formation of an excited molecule with a life of 10^{-6}—10^{-8} sec., it follows that the order of the decay process and both the luminous and the chemical phenomena connected with active nitrogen are likely to depend upon the total nitrogen pressure; this is evident, for if an excited molecule be not hit within this time it will most probably radiate its energy instead of transmitting it either as a whole or in part to another molecule.

A study of the decay of the glow in the presence of varying

quantities of other gases which do not react chemically with active nitrogen would also be of interest.

It is noticeable that Angerer (*loc. cit.*), working at pressures less than 1·0 mm., did not obtain the same slope for his $\sqrt{I}$-t curves in all his experiments, and, moreover, that the slope generally altered in the course of a single run; this is suggestive either of a change in the decay mechanism towards the end of the reaction or the influence of a heterogeneous reaction taking place at the same time (see Rayleigh, *Proc. Roy. Soc.*, 1912, *A*, **86**, 262).

This may be the explanation of the divergencies observed in the spectra developed by active nitrogen, and also of the recent claim of B. Lewis (*J. Amer. Chem. Soc.*, 1928, **50**, 27) that, when active nitrogen is mixed with active hydrogen at low pressures (0·4—0·02 mm.), ammonia is formed. He suggests that this is due to the reactions: (1) $N + H \longrightarrow NH$; (2) $NH + H_2 \longrightarrow NH_3$, but, as the present author has pointed out (*Nature*, 1928, **121**, 355), this theory is at variance with observations of Rayleigh (*Proc. Roy. Soc.*, 1911, *A*, **85**, 219) and of Willey and Rideal (J., 1927, 671) that ammonia *extinguishes* the glow of nitrogen and chemical action appears to be traceable; he fails to record such changes in the glow phenomena as would be anticipated. If, however, we are prepared to admit another mechanism of glow decay at low pressures and a form of chemically active nitrogen different from that obtained at higher pressures, an alternative explanation is easy. Since the number of collisions which a high-level excited molecule could suffer with neutral molecules during its life will diminish with the gas pressure, it follows that under the right conditions a chemically active molecule might be produced which, by virtue of its abnormal energy content as compared with the Rayleigh active nitrogen, would be capable of participating in reactions denied to the latter. The mechanism of Lewis's ammonia synthesis might then be regarded as (1) $N_2{}^1 + 2H_2 \longrightarrow N_2H_4{}^1$; (2) $N_2H_4{}^1 + H_2{}^1 \longrightarrow N_2H_6{}^1 \longrightarrow 2NH_3$. In this way his failure to obtain hydrazine is accounted for; the quasi-molecule first produced falls apart unless within its life it undergoes collision with an excited hydrogen *molecule* (see Phipps and Taylor, *Physical Rev.*, 1927, **29**, 309), and the reaction may take place without the direct participation of the nitrogen atoms and any changes of glow phenomena in consequence. It does not, moreover, appear valid to assume that such a reaction would occur only at low pressures. That nitrogen may momentarily exist in a more chemically active state than in the Rayleigh form is shown by the experiments of Jolibois and Lefebvre (*Compt. rend.*, 1927, **185**, 853), who found that the reaction $2CO + O_2 \longrightarrow 2CO_2$ in the discharge can be greatly furthered by the addition of nitrogen to the mixture.

Presumably the nitrogen is activated and undergoes second-type collisions with either the carbon monoxide or the oxygen or both, leading to the production of active forms of these substances. Moreover, Lowry (J., 1912, **101**, 1152; *Trans. Faraday Soc.*, 1913, **9**, 189) has presented evidence that a form of nitrogen oxidisable by ozone can be obtained by the spark discharge in air at atmospheric pressure, and although his observations may be due to the production of an unstable nitrogen oxide which reacts only with ozone and not with oxygen, the statement of Wendt and Grubb (*Chem. Met. Eng.*, 1920, **22**, 771), that the corona discharge in nitrogen at atmospheric pressure also gives rise to a *stable* variety of nitrogen which can react with oxygen and with hydrogen to give nitric oxide and ammonia respectively, leads still further to the view that nitrogen may exist in several chemically active forms. It may also be noticed that Usher and Venkateswaran (J., 1919, **115**, 613) have found that the nitrogen liberated during the electrolysis of sodium azide attacks mercury, a reaction suggestive of the formation of N_3 or N_6.

Summary.

Experiments upon the decay of the nitrogen afterglow show that the reaction is kinetically of the fifth order between 2 and 8 mm. pressure. Calculations applying kinetic theory to observations on the life of the glow show that, if the reaction be bimolecular in reality, the concentration of the glow-producing system, assumed to be atomic, is only 10^{-5}—10^{-6} of the chemically active nitrogen present in the same circumstances, a discrepancy overcome by assuming the process to represent an initial slow ternary reaction, $2N + N_2 \longrightarrow 2N_2$, followed by two rapid binary reactions. This theory accounts for the negative temperature coefficient of the glow-decay, and is considered (*a*) to furnish evidence that the glow and chemical activity in nitrogen represent separate and very variable stages in the complex deactivation process of a high-level molecule first formed from atoms, and (*b*) to explain the existence of other varieties of chemically active nitrogen reported from time to time and also divergencies in the spectroscopic and chemical characteristics of the Rayleigh form.

This work was carried out in the Laboratory of Physical Chemistry, Cambridge, in the summer and autumn of 1927, and the author's warmest thanks are due to Prof. T. M. Lowry, F.R.S., and Dr. E. K. Rideal and to all his colleagues for their constant advice and co-operation.

88 CROMWELL ROAD,
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CCXIII.—*The Chemistry of the Three-carbon System. Part XVII.* cyclo*Hexylideneacetone and* cyclo*Hexylidenemethyl Ethyl Ketone.*

By Alfred Henry Dickins, Wilfred Eynon Hugh, and George Armand Robert Kon.

The experiments described in the earlier papers of this series lead to the conclusion that tautomerism is to be expected in compounds of the general skeleton (I) or (II), subject to certain conditions

$$\text{(I.)}\quad {}^{R^{I}}_{R^{II}R^{III}CH}\!\!>\!C{:}CR^{IV}X \qquad\qquad {}^{R^{I}}_{R^{II}R^{III}C}\!\!>\!C{\cdot}CHR^{IV}X\quad\text{(II.)}$$

(X = electronegative activating group; R can be H, alkyl, aryl, or acyl groups.)

discussed there. The mobility and the point of equilibrium in any one system are the resultant of various structural factors; an estimate of the magnitude and relative importance of these factors is only possible on the strength of exact quantitative study of a variety of tautomeric systems and forms one of the principal objects of this series of researches. This task has been considerably facilitated by the elaboration of methods for the quantitative estimation of isomerides in mixtures (Linstead, J., 1927, 355; Linstead and May, *ibid.*, p. 2565), but their application is limited to cases where both individuals can be isolated in a state of purity, such as the pairs of unsaturated acids already investigated by Linstead (J., 1927, 362).

There are, however, compounds which have hitherto been isolated in one form possessing the functions of both the $\alpha\beta$- and the $\beta\gamma$-isomeride. With regard to ketones, Kon and Nutland (J., 1926, 3101) suggested that the two forms of the semicarbazone, when obtainable, are derived from the two individuals constituting the equilibrium mixture. Numerous attempts to isolate these individuals remained fruitless until the ketone (III) described by Kon (J., 1926, 1792) was synthesised. The compound obtained by the

$$H_2C\!<\!{}^{CH_2\cdot CH_2}_{CH_2-CH}\!\!>\!C{\cdot}CH_2{\cdot}COEt \qquad H_2C\!<\!{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}\!\!>\!C{:}CH{\cdot}COEt$$

(III.) (IV.)

action of zinc ethyl iodide on *cyclo*hexylideneacetyl chloride had properties indicating the structure (IV), notably an abnormally high molecular refraction; it gave a high-melting semicarbazone, identical with that obtained by Kon and Narayanan (J., 1927, 1546), and only a small quantity of the isomeric semicarbazone, m. p. 153° (Kon, *loc. cit.*). The ketone (III) was similarly obtained

from the corresponding acid and gave mainly the lower-melting semicarbazone. Under conditions avoiding the use of mineral acids and alkalis the ketones (III) and (IV) were obtained each practically free from its isomeride. The preparation of the corresponding *methyl ketones* (V) *and* (VI) was *more difficult, mixtures* being sometimes obtained under the most favourable conditions.

$$H_2C{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}{\gg}C\cdot CH_2\cdot COMe \qquad H_2C{<}\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}{>}C{:}CH\cdot COMe$$

(V.) (VI.)

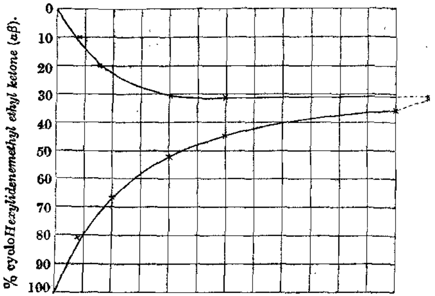
The ketone (V) is identical with that prepared by Wallach (*Annalen*, 1912, **394**, 376) and by Kon (J., 1921, **119**, 816), its semicarbazone, m. p. 145°, being identical with that obtained by previous investigators. The αβ-ketone (VI) gave a higher-melting semicarbazone identical with that isolated in minute amount by Birch, Kon, and Norris (J., 1923, **123**, 1361) and from which the new ketone could be regenerated, although a small amount of conversion into the βγ-form occurred even under very mild conditions.

The properties of the ketone (VI), like those of its higher homologue (IV), accord well with its constitution; it boils at a higher temperature than the βγ-form, has a higher density, and a much higher refractive index, the molecular refraction showing a considerable exaltation; its structure, moreover, was confirmed by oxidation with permanganate. The ketones (III) and (V) react quickly with alcoholic iodine chloride, whereas their αβ-isomerides show little reaction under the standard conditions adopted by Linstead and May (*loc. cit.*), thus allowing mixtures of isomerides to be analysed with considerable accuracy.

The equilibrium between the two pairs of ketones could therefore be studied quantitatively, different catalysts being used. In the *course of this work the astonishing observation was made that* although *cyclo*hexylideneacetone (and to a less extent the ketone IV) is, apparently, extremely sensitive to mineral acids *at the moment of its formation,* the pure substance is scarcely affected by them under the conditions described on p. 1635; indeed, the mobility of the substance is not of a high order, being much less than that of *iso*pulegone (Hugh, Kon, and Linstead, J., 1927, 2585). Such a discrepancy can only be attributed to an enhanced reactivity of the substance *in statu nascendi* in a manner analogous to that discussed by Goss and Ingold (J., 1925, **127**, 2776). Actually it was found that equilibration proceeded very slowly in presence of a small quantity of barium hydroxide, piperidine, or sulphuric acid. With sodium ethoxide in excess, equilibrium is completely established in 24 hours, the equilibrium mixture of (III) and (IV) containing 69% of the βγ-form; that obtained from (V) and (VI) contains

71% of the βγ-form. The crude ketones obtained by the condensation of *cyclo*hexanone with acetone and methyl ethyl ketone, respectively, should also possess this composition, as they are produced in the presence of sodium ethoxide. The numerous

FIG. 1.



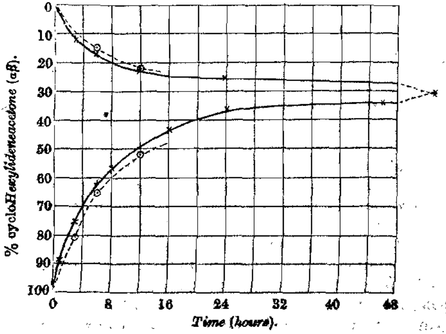


FIG. 2.

fractionations which are inevitable in these preparations, however, alter the proportion of the two isomerides; *e.g.*, a mixture of (III) and (IV) prepared as described by Kon (*loc. cit.*) contained 85% of the βγ-ketone, whereas a specimen of crude *cyclo*hexylacetone produced by the condensation of *cyclo*hexanone with ethyl sodioacetoacetate (see following paper) contained a slight excess of the αβ-ketone.

The point of equilibrium of the ketones now described is much nearer the $\alpha\beta$-side than that found by Linstead (*loc. cit.*) for the corresponding acids. A similar difference appears to exist between the diethylacrylic acids and the ketones derived from them (Linstead, *loc. cit.*), but further examples must be studied before any conclusion can be drawn from this observation.

The mobility of the two pairs of ketones in presence of sodium ethoxide in less than molecular quantity has been examined under comparable conditions; the results are shown in Figs. 1 and 2, from which it will be seen that the reaction appears to be a reversible unimolecular one; no attempt, however, has yet been made to follow this with great accuracy. It is hoped in the near future to develop an improved technique enabling quantitative comparisons to be made between the mobilities of different tautomeric substances under standard conditions. In the meantime, it appeared of interest to ascertain the effect of hydroxyl ions on the course of the equilibration. The addition of a slight excess of water to the mixture of the ketones and sodium ethoxide was found to have but little effect; it slightly retarded the change (Fig. 2, dotted curve).

The proof now supplied of the existence of pairs of individual substances forming an equilibrium mixture in presence of catalysts serves to emphasise the close analogy, foreshadowed in former communications, existing between substances exhibiting three-carbon tautomerism and those of the better-known keto-enol class.

EXPERIMENTAL.

cyclo*Hexylidenemethyl Ethyl Ketone* (IV).—The procedure described by Birch, Kon, and Norris (*loc. cit.*) was adopted, *cyclo*hexylideneacetyl chloride and zinc ethyl iodide being used. A fraction, b. p. 118—120°/25 mm., was obtained (yield, usually about 60%). It was treated with semicarbazide, a crude caseous semicarbazone being isolated. This, after being washed with petroleum to remove a small quantity of ester (which is always present, especially in the preparation of the $\beta\gamma$-ketone; compare Kon and Narayanan, J., 1927, 1546), was repeatedly crystallised from methyl alcohol, giving a less soluble portion, m. p. about 188°, and a more soluble portion from which a small amount of semicarbazone, m. p. 153°, was isolated; these were identical with the two compounds isolated by Kon and Narayanan (*loc. cit.*). When quite pure, the higher-melting compound formed fine prisms, m. p. 191°. The *ketone* regenerated from it with oxalic acid had b. p. 112°/22 mm.; $d_4^{18.1°}$ 0·93810, and $n_D^{18.1°}$ 1·48945; whence $[R_L]_D$ = 46·82 (calc., 45·84).

The amount of $\beta\gamma$-ketone formed could be reduced by using

acetic acid in place of mineral acid to liberate the ketone from the reaction product, and almost pure αβ-ketone was obtained by the following process: the acid chloride was slowly added to an excess of zinc ethyl iodide solution efficiently cooled in a bath of ice and calcium chloride, dry ether being added to prevent the solution from freezing. The product was immediately decomposed with ice, any rise of temperature being prevented, and carbon dioxide, scrubbed by passage through sodium carbonate, was bubbled through the solution until the decomposition was complete. The solution was then filtered, the sludge washed with ether, and the combined ethereal and benzene solutions were washed with water, shaken with saturated ammonium sulphate solution, dried, and distilled through an efficient column, finally under reduced pressure.

On several occasions the ketone so produced gave a low-melting semicarbazone which after several crystallisations formed long needles of constant m. p. 167°. The ketone regenerated from it appeared in every way identical with that obtained from the higher-melting form: b. p. 110—111°/18 mm., $d_4^{19.0^\circ}$ 0·937101, $n_D^{19.0^\circ}$ 1·48859; whence $[R_L]_D = 46{\cdot}82$; this gave on recombining with semicarbazide the high-melting semicarbazone. The form, m. p. 167°, may perhaps be a stereoisomeride of the latter.

Δ^1-cyclo*Hexenylmethyl Ethyl Ketone* (III).—The action of zinc ethyl iodide on Δ^1-*cyclo*hexenylacetyl chloride gave a ketonic fraction boiling some 4° lower than in the preceding case. Under ordinary conditions, this fraction gave a semicarbazone which was difficult to purify, although the form crystallising in plates, m. p. 153°, predominated and could be isolated by repeated crystallisation. It was practically the sole product when the isolation of the ketone was carried out with the aid of carbon dioxide. The *ketone* was regenerated from it more easily than in the case of the αβ-isomeride and boiled at 107°/22 mm.; it had $d_4^{17.5^\circ}$ 0·93020 and $n_D^{17.5^\circ}$ 1·47320, whence $[R_L]_D = 45{\cdot}89$ (calc., 45·84), and showed no change in optical properties after being kept in a sealed tube for 4½ months.

Equilibrium between the Ketones (III) *and* (IV).—May and Linstead's iodometric method (*loc. cit.*) was used, the conditions being the same as for pulegone and *iso*pulegone (Hugh, Kon, and Linstead, *loc. cit.*). The values obtained in 10 minutes with *M*/300-solutions in chloroform (mean of 3 concordant determinations in each case) were:

Mixture (% αβ)	0	10	25	50	75	90	100
% Addition	87·4	83·8	78·05	60·99	38·49	23·49	14·84

From the above data a reference curve was constructed similar to that used by Hugh, Kon, and Linstead (*loc. cit.*, p. 2590).

1. *With excess of sodium ethoxide.* 4 C.c. of the αβ-ketone were

kept at room temperature for 22 hours with 0·75 g. of sodium in 12·5 c.c. of alcohol; water was then added. The ketone isolated by means of ether boiled at 105—112°/18 mm. (the first two drops of distillate were rejected) and had $d_{4^\circ}^{17\cdot2^\circ}$ 0·934595 and $n_D^{17\cdot2^\circ}$ 1·47606; the % addition of iodine (mean of three concordant determinations) was 73·85, corresponding to 31·5% of αβ-ketone. The experiment was simultaneously *carried out* with the pure βγ-ketone; the product had b. p. 116—124°/24 mm., $d_{4^\circ}^{18\cdot2^\circ}$ 0·931576, and $n_D^{18\cdot1^\circ}$ 1·47613; the % addition of iodine was 74·6, corresponding to 30·5% *of* αβ-*ketone. The point of equilibrium is therefore* approximately 31% αβ : 69% βγ.

2. *With insufficient sodium ethoxide.* 2 C.c. of each ketone were pipetted into a 50 c.c. graduated flask, 20 c.c. of a 1% solution (by weight) of sodium in ethyl alcohol were added, and the mixture was made up to 50 c.c. with alcohol. After the requisite time, the ketone was isolated as above and its composition estimated iodometrically (the physical properties were also determined as a check but are not quoted):

Initial material: αβ-ketone.

Time (hrs.)	3	8	16	24	48
% Iodine addition	33·11	48·05	49·28	65·43	70·51
% αβ-Ketone	81	66	52·5	45	37

Initial material: βγ-ketone.

Time (hrs.)	3	6	16	24
% Iodine addition	84·3	80·42	74·5	74·02
% αβ-Ketone	10	20	30·5	31

These results are expressed graphically in Fig. 1.

3. *With sulphuric acid.* 2 C.c. of each ketone were mixed with 10 c.c. of *N*-sulphuric acid, made up to 50 c.c. with alcohol, and kept for 16 hours at room temperature. The αβ-ketone underwent about 7·5% conversion; no change could be detected in the βγ-ketone.

4. *With piperidine.* Similar experiments were performed, 10 c.c. of *M*/2-alcoholic piperidine being used in place of sulphuric acid. There was no measurable change in the βγ-ketone and the αβ-ketone underwent 8·5% conversion.

Direct Condensation of cyclo*Hexanone and Methyl Ethyl Ketone.*—A sample of the ketone prepared by Kon's method (*loc. cit.*) and having properties similar to those recorded was found to contain approximately 84·5% *of the* βγ-ketone.

Condensation of the βγ-*Ketone with Ethyl Sodiomalonate.*—This condensation was carried out exactly as described by Norris and Thorpe (J., 1921, **119**, 1199). The dihydroresorcinol ester was formed in good yield, but was only obtained as a viscous liquid giving a dark red colour with ferric chloride. It was therefore

hydrolysed with barium hydroxide to cyclo*hexane*spiro-4-*methyl*-cyclo*hexane*-3 : 5-*dione*, which crystallised from dilute methyl alcohol in clusters of needles, m. p. 179° (Found: C, 74·0; H, 9·3. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·4%).

cyclo*Hexylideneacetone* (VI).—This compound was prepared from *cyclo*hexylideneacetyl chloride and zinc methyl iodide by the modified procedure given on p. 1634, otherwise equilibrium mixtures were always obtained; indeed, the preparation sometimes gave a mixture without ascertainable reason. Esters do not appear to be formed when zinc methyl iodide is employed and the ketone can be obtained sufficiently pure by repeated fractionation of the reaction product. The fraction boiling at 89°/12·5 mm. had $d_4^{19.0°}$ 0·94931 and $n_D^{19.0°}$ 1·49128, whence $[R_L]_D = 42·16$ (calc., 41·22); this was used for the reference curve. The *semicarbazone* obtained from it was much less soluble than that of the βγ-ketone; it melted in the crude state at 169—170° and formed plates, m. p. 180°, after repeated crystallisation from methyl alcohol (Found: C, 61·8; H, 8·9. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·8%). The *ketone* can be regenerated from it *practically* unchanged, b. p. 95°/17 mm., $d_4^{17.3°}$ 0·94673, $n_D^{17.3°}$ 1·48917, although the iodine absorption of the product obtained is slightly higher than that of the ketone purified by fractionation. The semicarbazone obtained on treating the regenerated product with semicarbazide had no definite crystalline form and melted much too low.

The odour of the new ketone is sharper and less pleasant than that of its isomeride. The ketone develops a colour with alcoholic ferric chloride only on standing. The structure of the ketone was confirmed by oxidation, the ketone being suspended in ice-water and a slight excess of 3% aqueous potassium permanganate slowly added with constant shaking; ether extraction of the filtered solution gave a good yield of *cyclo*hexanone, which was identified in the form of its semicarbazone, m. p. 165—166°.

Δ¹-cyclo*Hexenylacetone* (VI).—This ketone was prepared from *cyclo*hexenylacetyl chloride and zinc methyl iodide in the same way as the αβ-ketone. It gave a crystalline semicarbazone, m. p. 136—137° (crude), 145° (after one crystallisation from methyl alcohol), and the ketone regenerated from this had properties agreeing with those recorded by Wallach (*loc. cit.*), namely, b. p. 83°/12 mm., $d^{18.8°}$ 0·93751, $n_D^{18.8°}$ 1·47310; whence $[R_L]_D = 41·33$. A homogeneous, crystalline semicarbazone was obtained from the regenerated ketone.

Equilibrium between Ketones (V) *and* (VI).—It was first necessary to ascertain whether the αβ-ketone, purified by distillation only, could be used, in view of the fact that it is partly equilibrated on

regeneration from the semicarbazone. If the lower iodine absorption of this crude ketone is due to the presence of saturated impurities, this should be detected by ascertaining whether the same final equilibrium mixture is formed from the crude as from the regenerated ketone. It was found that the difference between the iodine values of the two samples diminished considerably on equilibration and it appeared best to use a carefully fractionated specimen of αβ-ketone for the reference curve and the points on the αβ-side of the curve in Fig. 2; the regenerated ketone was used for ascertaining the final equilibrium and points near it (16, 24, and 48 hours); and a regenerated sample of *cyclo*hexenylacetone was used throughout.

The reference curve was constructed as in the preceding case, the values obtained being as follows:

Mixture (% αβ)	0	10	25	50	75	90	100
% Addition	83·7	80·7	74·7	60·5	40·7	26·8	15·8

1. *With excess of sodium ethoxide.* The experiment was carried out as described on p. 1635, except that the reaction was allowed to proceed for 24 hours. The product from the αβ-ketone had b. p. 88—94°/19 mm., $d_{4°}^{16·2°}$ 0·94446, and $n_D^{16·2°}$ 1·47633; the % iodine addition (mean of three concordant determinations) was 73·37, corresponding to 28·5% of αβ-ketone. The product from the βγ-ketone had b. p. 90—96°/17 mm., $d_{4°}^{16·4°}$ 0·94446, and $n_D^{16·4°}$ 1·47693; the % iodine addition was 73·10, corresponding to 29·0% of αβ-ketone.

2. *With insufficient sodium ethoxide.* The method of procedure was the same as for the higher homologues (p. 1635). Results:

Initial material: αβ-ketone.

Time (hrs.)	1	3	6	8	16	24	48
% Iodine addition	28·0	39·2	50·9	54·8	64·6	68·0	70·2
% αβ-Ketone	89·0	76·8	62·5	57·5	43·0	37·5	34·0

Initial material: βγ-ketone.

Time (hrs.)	3	6	12	24
% Iodine addition	80·8	78·7	75·8	74·4
% αβ-Ketone	12·0	17·0	23·5	26·5

These results are shown graphically in Fig. 2.

3. *With sodium hydroxide.* The catalyst used was prepared by dissolving 2 g. of sodium in 200 g. of alcohol, 10 c.c. of water being then added; 20 c.c. of this solution were used as before. The results were:

Initial material.	Time (hrs.).	% Iodine addition.	% αβ-Ketone.
αβ-Ketone	3	35·6	80·5
,, ...	6	48·1	66·0
,, ...	12	58·2	52·5
βγ-Ketone	6	79·5	16·0
,, ...	12	76·5	22·5

These results are marked ⊙ on Fig. 2.

The authors' thanks are due to the Royal Society and the Chemical Society for grants which have partly defrayed the cost of this investigation.

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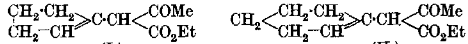
CCXIV.—*The Condensation of Ketones with Ethyl Acetoacetate.*

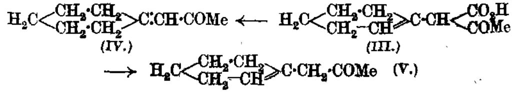
By LEONARD GEORGE JUPP, GEORGE ARMAND ROBERT KON, and EDWARD HUBERT LOCKTON.

THE object of the present investigation was the preparation of esters such as (I) and (II) which should be of considerable interest



(I.) (II.)

from the point of view of three-carbon tautomerism. Ethyl *iso*propylideneacetoacetate, CMe_2:C(COMe)·CO_2Et, had already been prepared by Merling and Welde (*Annalen*, 1909, **366**, 119) by condensing ethyl acetoacetate with acetone. Their method, however, fails when *cyclo*hexanone is used in place of acetone, *cyclo*hexenyl-*cyclo*hexanone being the sole product. We therefore tried the action of *cyclo*hexanone on ethyl sodioacetoacetate and obtained evidence of a reaction in the desired direction, but the ester (II) was formed in insignificant amount and it was practically impossible to separate it from the large quantities of other products such as *cyclo*hexenyl-*cyclo*hexanone. The acid portion of the reaction product contained a considerable quantity of the corresponding acid (III), which could be readily obtained pure. This acid cannot be esterified by ordinary methods, being either unattacked or converted into some compound formed by a secondary change. It is otherwise remarkably stable and can be kept unchanged for many months. It gives off carbon dioxide just above its melting point and yields a mixture of *cyclo*hexylideneacetone (IV) (Dickins, Hugh, and Kon, preceding paper) and *cyclo*hexenylacetone (V), the former predominating:

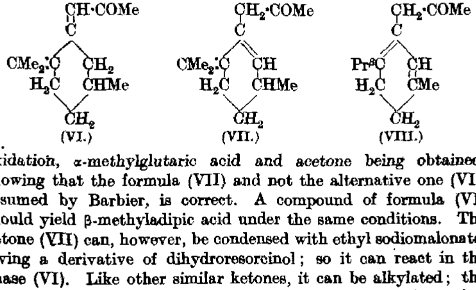


(IV.) (III.) (V.)

The preferential production of the αβ-ketone (IV), which is less stable than the βγ-ketone, from an acid having the βγ-structure is certainly remarkable and requires further investigation.

The ketones (IV) and (V) were present in quantity, approximately in the proportions of the equilibrium mixture (Dickins, Hugh, and Kon, *loc. cit.*), in the neutral products of the original condensation. The yield was increased at the expense of the acid (III) by adding water (1 mol.) to the reaction mixture after 24 hours and continuing the heating for a few hours longer—this constitutes the best method of preparing the equilibrium mixture in quantity. *cyclo*Pentenylacetone could not be prepared by a similar process, the only ketone produced in the condensation of *cyclo*pentanone with ethyl sodioacetoacetate being *cyclo*pentylidene*cyclo*pentanone; the ester (I) could not be isolated, although a minute quantity of the corresponding acid was obtained. The oxidation of this acid showed that, unlike the acid (III), it had an $\alpha\beta$-unsaturated structure; this difference is analogous to that already observed in the malonic acids (Kon and Speight, J., 1926, 2787).

Finally, pulegone and piperitone were condensed with ethyl acetoacetate. The principal compound obtained from the former is the ketone (VII) prepared by Barbier (*Compt. rend.*, 1898, **127**, 870). The structure of this compound was confirmed by



(VI.) (VII.) (VIII.)

oxidation, α-methylglutaric acid and acetone being obtained, showing that the formula (VII) and not the alternative one (VI), assumed by Barbier, is correct. A compound of formula (VI) should yield β-methyladipic acid under the same conditions. The ketone (VII) can, however, be condensed with ethyl sodiomalonate, giving a derivative of dihydroresorcinol; so it can react in the phase (VI). Like other similar ketones, it can be alkylated; the alkyl derivative gives the same oxidation products as the parent substance. The product obtained from piperitone has not been fully investigated, but by analogy it probably has the structure (VIII).

EXPERIMENTAL.

Condensation of cyclo*Hexanone with Ethyl Sodioacetoacetate.*—Ethyl acetoacetate (260 g.) was added to a solution of 46 g. of sodium in 600 c.c. of alcohol, followed by 196 g. of *cyclo*hexanone; the mixture was heated under reflux for 24 hours. Water was added and the oil was taken up in ether, washed, dried, and distilled

under reduced pressure (Neutral Oil A). The aqueous layer was strongly acidified with dilute sulphuric acid and again thoroughly extracted with ether; this extract on being dried and evaporated gave a solid (B).

The oil A gave on fractional distillation ethyl acetate, *cyclo*hexanone, a considerable fraction, b. p. 68—94°/17 mm., and a fraction boiling up to 120°/17 mm. The last two fractions on refractionation usually gave about 40 g., b. p. 84—88°/11 mm., and fractions, b. p. 79—83° and 89—95°. All these had the characteristic odour of *cyclo*hexenylacetone and gave a caseous semicarbazone from which the semicarbazone, m. p. 145° (Wallach, *Annalen*, 1913, **396**, 376; Dickins, Hugh, and Kon, *loc. cit.*) was isolated. Titration with iodine chloride (kindly carried out by Mr. W. E. Hugh) showed that the main fraction, $d_{4^\circ}^{17.6^\circ}$ 0·94053, n_D 1·47555, had a composition closely approximating to that of the equilibrium mixture, namely, 70·5% of the βγ-form (72·7% addition) (Dickins, Hugh, and Kon, *loc. cit.*), and that there was a slight excess of the αβ-form in the highest fraction (53·5% βγ). The yield of equilibrium mixture can be considerably increased by adding water to the condensation product of *cyclo*hexanone and ethyl sodioacetoacetate and continuing the boiling for a further 6 hours. In one experiment, 21·5 g. of ketone (32%) were obtained from 65 g. of ethyl acetoacetate in this way.

Progressive refractionation of the higher fractions of the oil A gave a quantity of *cyclo*hexenyl*cyclo*hexanone (Wallach, *Annalen*, 1911, **381**, 95; Kon and Nutland, J., 1926, 3101), and a very small amount, seldom more than 1 g., of an oil, b. p. 135°/20 mm., giving an intense red-violet colour with alcoholic ferric chloride and consisting of the *ester* (II) (Found : C, 68·8; H, 8·6. $C_{12}H_{18}O_3$ requires C, 68·6; H, 8·6%). It was characterised by the *semicarbazone*, m. p. 141° (Found : C, 58·2; H, 8·0; N, 15·5. $C_{13}H_{21}O_3N_3$ requires C, 58·4; H, 7·9; N, 15·7%). It was not possible to isolate a sufficient quantity of the ester to confirm its constitution.

cyclo*Hexenylacetoacetic acid* (III). The solid acid B (45—60 g.), after recrystallisation from benzene–light petroleum, formed needles, m. p. 121° (decomp.), consisting of Δ¹-cyclo*hexenylacetoacetic acid*. The acid can also be recrystallised from dilute alcohol, but aqueous solvents should be avoided, as the acid readily loses carbon dioxide on boiling with water (Found : C, 65·9; H, 8·0. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·8%. Titration : Found, 19·8 c.c. NaOH; calc. for monobasic acid, 19·7 c.c.). The *semicarbazone*, m. p. 196°, crystallised from methyl alcohol (Found : C, 55·1; H, 7·2; N, 17·2. $C_{11}H_{17}O_3N_3$ requires C, 55·2; H, 7·2; N, 17·5%).

Oxidation. The acid, dissolved in an excess of aqueous sodium

hydrogen carbonate, was treated with a slight excess of 3% aqueous potassium permanganate. The filtered solution gave to ether no neutral oxidation products, but after being acidified and re-extracted, it gave oxalic and adipic acids, which were separated by means of benzene. These two acids were also obtained when the acid (*III*) was oxidised with ozone in chloroform solution.

Action of heat. When heated under reduced pressure just above its melting point, the acid gave an almost theoretical yield of a ketone, b. p. 86—87°/13 mm., $d_4^{17.8°}$ 0·94250, $n_D^{17.8°}$ 1·48810, which was isolated from the distillate by means of ether. The iodine absorption of the ketone determined by Mr. Hugh was 41·3, corresponding to 74·3% of the αβ-form (IV). The semicarbazone obtained from it was caseous, but on repeated crystallisation from methyl alcohol gave the characteristic plates of *cyclo*hexylideneacetone-semicarbazone, m. p. 180°.

Attempts to esterify the acid (III). Methyl sulphate and sodium hydroxide had no action on the acid.

The silver salt, boiled over-night with an excess of methyl iodide in dry ether, gave an unsaturated substance, isomeric with (III), which did not give the expected colour with ferric chloride, was sparingly soluble in ether, and crystallised from dilute alcohol in plates, m. p. 177°; it did not effervesce with sodium hydrogen carbonate, although it dissolved in alkalis and was reprecipitated by acids (lactone ?) (Found: C, 65·5, 65·9; H, 7·9, 7·7. $C_{10}H_{14}O_3$ requires C, 65·7; H, 7·8%).

By the methyl-alcoholic hydrogen chloride method, from 5 g. of the acid were obtained 2 g. of an isomeric *substance* which crystallised from dilute methyl alcohol in long needles, m. p. 80° (Found: C, 65·8; H, 7·8%); it had no acid properties and gave a slight colour with ferric chloride (the liquid filtrate obtained from the original distillate gave a marked colour and had an odour of *cyclo*hexenylacetone). The same compound was produced when the acid (3 g.) was kept with methyl alcohol (10 c.c.) and concentrated sulphuric acid (3 c.c.) for 60 hours.

Other attempts to prepare the ester (II). (1) Ethyl *cyclo*hexenylmalonate (48 g.), prepared from the pure acid (Kon and Speight, *loc. cit.*), was added to 4·6 g. of "molecular" sodium in benzene, together with two drops of alcohol to start the reaction; 16 g. of acetyl chloride were added after an hour and the mixture was heated for 2 hours. Water was then added and the benzene solution was washed, dried, and evaporated; on distillation, 8 g. of *ethyl* Δ^1-*cyclohexenylacetylmalonate*, b. p. 161°/19 mm., were obtained (Found: C, 63·8; H, 7·8%) and characterised by its *semicarbazone*, m. p. 178° (Found: C, 56·6; H, 7·6; N, 12·2. $C_{16}H_{25}O_5N_3$ requires C, 56·6;

H, 7·4; N, 12·4%). When the new ester was warmed with an excess of sodium ethoxide for 4 hours, ethyl *cyclo*hexenylmalonate and ethyl acetate were produced.

(2) Ethyl chloroformate failed to condense with the sodio-derivative of *cyclo*hexenylacetone in dry benzene.

(3) Ethyl *cyclo*hexenylmalonate (120 g.) was heated for 4 hours with 28 g. of potassium hydroxide in 500 c.c. of alcohol. The neutral solution was diluted with water, extracted with ether, acidified, and re-extracted. The crude acid-ester obtained was treated with an excess of thionyl chloride and distilled, giving 46 g. of an acid-chloride-ester, b. p. 151°/19 mm., and 15 g. of a high fraction probably containing the diacid chloride. The acid-chloride-ester, when treated with an excess of zinc methyl iodide (Blaise and Maire, *Ann. Chim. Phys.*, 1908, **15**, 556), was apparently reconverted into the acid-ester and the desired ketonic ester was not obtained.

When *cyclo*hexanone was condensed with ethyl acetoacetate in presence of zinc chloride and acetic anhydride, *cyclo*hexenylacetone was obtained. With dry sodium ethoxide or sodium methoxide prepared by Komppa's method (*Annalen*, 1909, **368**, 137), the products were the same as with alcoholic sodium ethoxide, and " molecular " sodium in benzene gave no measurable quantity of the ester (II) and a poor yield of the other products.

Condensation of cyclo*Pentanone with Ethyl Sodioacetoacetate*.—The reaction was carried out as described on p. 1639 with half-molecular quantities. No *cyclo*pentenylacetone was isolated from the neutral fraction, *cyclo*pentylidene*cyclo*pentanone (Wallach, *Ber.*, 1896, **29**, 2963; Kon and Nutland, *loc. cit.*) was obtained in quantity, but none of the desired ester appeared to be formed. The acid product consisted of cyclo*pentylideneacetoacetic acid* (1·5 g.), which crystallised from dilute alcohol in needles, m. p. 137° (decomp.) (Found: C, 64·0; H, 7·2. $C_9H_{12}O_3$ requires C, 64·2; H, 7·2%. Titration: Found, 20·4 c.c. *N*/10-NaOH; calc., 20·6 c.c.). The acid in chloroform solution was oxidised with ozone and the ozonide decomposed with water as usual; *cyclo*pentanone and oxalic acid were isolated.

Ethyl iso*Propylideneacetoacetate*.—This ester was prepared as described by Merling and Welde (*loc. cit.*) in order to study its behaviour on alkylation. The ester had b. p. 103°/18 mm., $d_4^{21\cdot0^\circ}$ 0·96308, $n_D^{21\cdot0^\circ}$ 1·45583, whence $[R_L]_D = 46\cdot52$ (calc., 44·96). The *semicarbazone* melted at 247° after crystallisation from alcohol (Found: C, 52·8; H, 7·8; N, 18·2. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·6; N, 18·5%). All attempts to methylate the ester with the aid of " molecular " sodium in solvents failed, and in the presence

of alcohol the methylated ester immediately underwent fission, as already observed by Merling and Welde, giving ethyl trimethylacrylate, $d_4^{21\cdot 0^\circ}$ 0·97812, $n_D^{21\cdot 0^\circ}$ 1·45802, whence $[R_L]_D = 41{\cdot}02$ (calc., 40·33). The structure of this ester was confirmed by oxidation with ozone, acetone being obtained.

Δ^1-*Pulegenylacetone* (VII).—This ketone, b. p. 149—153°/21 mm., m. p. 73°, was prepared either by condensing pulegone with ethyl sodioacetoacetate or by the process used by Barbier (*loc. cit.*), the former giving 29 g. and the latter 55 g. of ketone from 1 g.-mol. of pulegone. The corresponding keto-ester or acid was not isolated in either preparation. The *semicarbazone*, m. p. 187°, crystallised from benzene (Found: C, 67·2; H, 9·4. $C_{14}H_{23}ON_3$ requires C, 67·4; H, 9·3%). The ketone in chloroform was oxidised with ozone, and the ozonide decomposed with dilute sulphuric acid; acetone and α-methylglutaric acid were isolated and identified as usual, the constitution now assigned to the ketone thus being confirmed.

α-*Methyl*-α-Δ^1-*pulegenylacetone*.—Pulegenylacetone (19·2 g.) was added to "molecular" sodium (2·3 g.) in dry ether (50 c.c.) and when the vigorous reaction had subsided an excess of methyl iodide was introduced; the mixture was finally refluxed for 2 hours. The ketone was isolated in the usual way and the fraction, b. p. 149—154°/20 mm., was treated with semicarbazide; the *semicarbazone* melted at 191° after crystallisation and depressed the melting point of the semicarbazone of pulegenylacetone (Found: C, 68·4; H, 9·4. $C_{15}H_{25}ON_3$ requires C, 68·4; H, 9·6%). The *ketone* regenerated from it by means of oxalic acid in a current of steam had b. p. 150°/21 mm., $d_4^{21\cdot 2^\circ}$ 0·94694, $n_D^{21\cdot 2^\circ}$ 1·49347, whence $[R_L]_D = 64{\cdot}39$ (calc., 63·73). The new ketone gave on oxidation with ozone the same products as the parent substance.

Condensation of Pulegenylacetone with Ethyl Sodiomalonate.—The ketone (19·2 g.) was added to a mixture of ethyl malonate (16 g.) and sodium (2·3 g.) dissolved in alcohol (40 c.c.) and the whole was heated on the steam-bath for 2 hours. Water was then added and the solution was extracted with ether to remove neutral impurities, acidified, and re-extracted. The crude keto-ester obtained was hydrolysed by boiling for 20 hours with 90 g. of barium hydroxide in 720 c.c. of water. The hot solution was acidified and filtered, then an excess of concentrated hydrochloric acid was added and the solution again boiled for 15 minutes. On cooling, the *dihydroresorcinol* derivative separated (2·5 g.); it crystallised from alcohol in needles, m. p. 130°, and gave a reddish-violet colour with ferric chloride (Found: C, 76·7; H, 9·6. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·5%).

Condensation of Piperitone with Ethyl Acetoacetate.—Piperitone (from eucalyptus oil) was condensed with ethyl acetoacetate in the same way as pulegone; the yields of ketone $C_{13}H_{20}O$ were about 10% by Barbier's method and 6% in presence of sodium ethoxide. No keto-ester appeared to be formed. The ketone was isolated in the form of *semicarbazone*, m. p. 217° after crystallisation from alcohol (Found: C, 67·5; H, 9·3. $C_{14}H_{23}ON_3$ requires C, 67·4; H, 9·3%). The *ketone* regenerated from it had b. p. 155°/20 mm., $d_{4^\circ}^{21\cdot8^\circ}$ 0·95821, $n_D^{21\cdot8^\circ}$ 1·49610, whence $[R_L]_D = 60\cdot59$. The properties of this substance have not yet been fully investigated.

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CCXV.—*Properties of Conjugated Compounds. Part V. The Hydrogenation of Certain Extended Heterogeneous Systems.*

By JOHN TREVOR EVANS and ERNEST HAROLD FARMER.

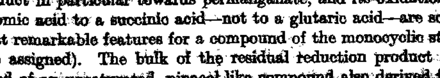
THE literature bearing on hydrogen addition to conjugated compounds containing simple butadienoid, extended or heterogeneous systems indicates an overwhelming and apparently exclusive tendency to the $\alpha\delta$-attachment of hydrogen. Observations on the attachment of other addenda (see the previous papers of this series) render it certain that, although terminal products may frequently arise in the hydrogenation process, they cannot be the exclusive *primary* products of addition, unless (*a*) propenoid activity is absent as a feature of the hydrogenation process under all conditions, or (*b*) the position of equilibrium connecting alternative propenoid forms (as determined by the groups attached to the three-carbon chain) favours under all conditions of hydrogenation, excluding catalytic processes, the formation of terminal products. Experiments on the hydrogenation of different varieties of conjugated compounds have shown that terminal addition of hydrogen is not universal, and the hydrogenation of certain heterogeneous substituted butadienes will now be described.

It has been recorded by one of us (*J.*, 1923, **123**, 2531, *et seq.*) that muconic acid, its esters and its $\alpha\alpha'$-dihalogenated (substituted) derivatives are converted by hydrogenation into Δ^β-dihydro-compounds. In all the experiments with these substances the most

painstaking search has failed to reveal the presence of any trace of a Δ^{α}-compound. To the methods previously employed, in which the reducing medium was strongly acid or alkaline, is now added that of reduction in neutral solution by means of aluminium amalgam. Ethyl muconate may be hydrogenated quite readily in this way, but the sole product is again the Δ^{β}-compound. One of the objects of this prolonged series of reductions in the muconic group is to establish beyond doubt that the muconic system, as representing a butadiene chain symmetrically substituted by carbonyl, yields exclusively (so far as separative methods indicate), with hydrogen generated in the usual different ways, a product hydrogenated at the $\alpha\delta$-carbon atoms. It has been sought to compare the hydrogenation product of the analogous, but unbalanced, heterogeneous compound $CH_3\cdot CO\cdot CH\colon CH\cdot CH\colon CH\cdot CO_2H$ with that of muconic acid: up to the present, however, the synthesis of this ketonic acid in adequate quantities has resisted our efforts. The butadiene monocarboxylic acids and ketones, on the other hand, are readily prepared in quantity, and the differentiation to be anticipated on polar grounds between their hydrogenated products and those of muconic derivatives is found in practice.

Hydrogenation of crotylideneacetone ($CHMe\colon CH\cdot CH\colon CH\cdot COMe$) *in moist ethereal solution by aluminium amalgam* yielded upwards of 80% of a compound derived from two molecules of the ketone. This substance, doubtless a cyclised form of the diketone (I), absorbed four atoms of hydrogen when catalytically hydrogenated, and yielded by ozone oxidation acetaldehyde together with an aldehydic oil: the latter, not satisfactorily oxidisable with permanganate, yielded succinic acid when heated with a solution of chromic acid.

(I.)



(II.)

To this main reduction product, closely resembling the bimolecular reduction products of mesityl oxide and phorone, the formula (II) is assigned (although the very great resistance of the mesityl oxide product in particular towards permanganate, and its oxidation by chromic acid to a succinic acid—not to a glutaric acid—are somewhat remarkable features for a compound of the monocyclic structure assigned). The bulk of the residual reduction product consisted of an unsaturated, pinacol-like compound also derived from two molecules of the ketone: its constitution is uncertain. Simple dihydro-ketones were absent, or present only in very small proportion.

Sorbic acid yielded, when reduced in moist ethereal solution with aluminium amalgam, a mixture of Δ^{β}- and Δ^{γ}-dihydrosorbic acids ($CH_2Me{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2H$ and $CHMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, respectively). A similar mixture was produced by reduction by the action of (*a*) aluminium amalgam on an aqueous neutral solution of sodium sorbate, (*b*) sodium amalgam on a glacial acetic acid solution of sorbic acid, and (*c*) sodium amalgam on an aqueous solution of sodium sorbate through which carbon dioxide was being passed. We are indebted for the observation (*c*) to Mr. Goldberg, who first observed, while endeavouring to obtain pure Δ^{β}-dihydrosorbic acid by a slight modification of Fittig's sodium-amalgam method, that a reduction product of sorbic acid yielded acetaldehyde on ozonisation and therefore could not be the homogeneous Δ^{β}-acid. An approximate estimate (representing a lower limit) of the Δ^{γ}-acid in these acid mixtures was made by estimating the succinic acid derived by permanganate oxidation in neutral solution. Under the conditions of the first three of the above-mentioned methods of reduction the proportions of the Δ^{γ}-acid were approximately 35, 40, and 30%, respectively. The *oxidation fragment complementary to succinic* acid—acetic acid—was recognisable, although mixed with propionic *acid arising from the Δ^{β}-acid; the malonic acid theoretically* derivable from the Δ^{β}-acid had, however, been entirely converted into acetic acid.

Although the orientation of the hydrogenation products of sorbic acid appears very similar under the different experimental conditions, it is possible that in other instances the mode of generating hydrogen (as distinct from the capacity of the medium to bring about a $\alpha\beta$–$\beta\gamma$ change after the addition; compare the recent reduction of cinnamylidenefluorene by Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 123, in which the 1 : 4- is converted into the 3 : 4-dihydro-compound in alkaline solution) has an effect on the orientation of the reduction products. Such a differential effect might be a reflexion, wholly or partly, of differences in the condition of the attacking hydrogen. Whether this be so or no, a major influence on the orientation of the products would seem to be that of the groups attached to the original butadiene system, as exemplified by the four isomeric methylbutadiene-α-carboxylic acids and the three toluic acids, some of which are at present being examined.

EXPERIMENTAL.

Hydrogenation of Ethyl Muconate in a Neutral Medium.—Ethyl muconate (28 g.), dissolved in moist ether, was left in contact with amalgamated aluminium foil for 16 hours. The ester obtained from the filtered product (24 g.) distilled at 127°/12 mm., leaving a small

residue, and was *pure ethyl* Δ^{β}-*dihydromuconate*, *homogeneity* being established by the tests: (i) careful oxidation with dilute neutral permanganate at 0° yielded no succinic acid; (ii) the amide formed almost quantitatively with concentrated aqueous ammonia was the homogeneous amide of the Δ^{β}-ester (m. p. 212—214°); (iii) the acid derived by rapid hydrolysis with hydrochloric or dilute sulphuric acid was found on careful fractional crystallisation to consist only of Δ^{β}-dihydromuconic acid, m. p. 195°.

Hydrogenation of Crotylideneacetone.—The ketone (Meerwein, *Annalen*, 1908, **358**, 85) (40 g.) was dissolved in moist ether and left in contact with amalgamated aluminium foil for 16 hours. Filtration of the product and evaporation of the solvent yielded a colourless oil, from which four fractions were obtained: (i) 1—1½ g., b. p. below 80°/19 mm.; (ii) 2—3 g., b. p. 80—158°/19 mm.; (iii) 18 g., b. p. 158—168°/17 mm.; (iv) 8 g., b. p. 168—178°/17 mm. Fractions (iii) and (iv) were separately submitted to steam distillation: almost the whole of the former and the major portion of the latter distilled. The non-volatile material remaining in the mother-liquors was obtained, on extraction, as a very viscid liquid (2 g.), b. p. 175—180°/16 mm.: it possessed some of the characteristics of an unsaturated pinacol, but its exact constitution was not determined. The combined aqueous distillates yielded a colourless, somewhat viscid liquid (b. p. 169—178°/23 mm.) which absorbed hydrogen readily (4 atoms per molecule on the formula assigned) when reduced catalytically, and arose apparently in strictly analogous fashion to the bimolecular reduction products of mesityl oxide and phorone. In view of its degradation products it is regarded as *5-acetyl-1'-methyl-3 : 4-dipropenyl*cyclo*pentan-1-ol* (II) (Found: C, 75·3; H, 9·6. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%). An examination of the low-boiling portion of the reduction product (about 3 g.) derived from fractions (i) and (ii) showed it to be non-ketonic; it probably consisted of methylbutadienylcarbinol, but this constitution has not been confirmed.

*Oxidation of Acetylmethyldipropenyl*cyclo*pentanol.*—The substance (2 g.), dissolved in chloroform (30 c.c.), was submitted to ozonisation for 6 hours. Removal of the solvent at reduced pressure yielded a pale yellow viscous ozonide, which was decomposed by gentle heating with water (30 c.c.). The vapours evolved during the decomposition were passed into aqueous *p*-nitrophenylhydrazine hydrochloride, with which they yielded a bulky crystalline precipitate of acetaldehyde-*p*-nitrophenylhydrazone (m. p. 126° after recrystallisation from aqueous alcohol; mixed m. p. with authentic specimen, 126°). The aqueous liquor contained an oily aldehydic product which yielded a syrupy acid when cautiously oxidised with dilute perman-

ganate at 0°. This acid, the homogeneity of which was doubtful, was not further investigated. Since regulated oxidation of the *cyclo*pentanolones derived from 1 : 4-diketones appears rarely to be successful, the customary drastic reagent (chromic acid) for *cyclo*pentanolone degradation was employed. A cyclic aldehyde derived by ozonisation of a substance of formula (II) should yield succinic acid on oxidation with chromic acid.

Accordingly the ketone (10 g.), dissolved in glacial acetic acid (60 c.c.), was ozonised for 24 hours. To the product, diluted with a further 100 c.c. of acetic acid, a solution of chromic acid (100 g.) in 50% aqueous acetic acid (160 c.c.) was gradually added. The reaction, which at first required moderating by cooling, was completed by gently refluxing the mixture for 1 hour. Chromium was then removed from the cooled oxidation mixture by addition of alkali and filtration. The filtrate was evaporated to dryness, and the residue, after being acidified and again evaporated, was finely powdered and extracted with acetone. The extract gave a considerable amount of succinic acid.

A compound of formula (II) should give rise, by the degradation of a diozonide, to two molecules of acetaldehyde, or on oxidation with permanganate to two molecules of acetic acid. Attempts to estimate the acetic acid produced by degradation were made, but although considerable quantities of the crude acid were obtained, the presence of volatile acidic impurities rendered the figures valueless.

Hydrogenation of Sorbic Acid.—(a) *By aluminium amalgam in a neutral medium.* Amalgamated aluminium foil was allowed to react for 24 hours with a solution of sorbic acid in a large volume of moist ether. The filtered solution was washed once with water, dried, and evaporated. The oily residue was dissolved in light petroleum, and the solution twice cooled to −25° and decanted. Some unchanged sorbic acid was thus separated. After removal of the solvent the residual oily acid distilled at 96—98°/12 mm., leaving a trace of sorbic acid and a quantity of viscous liquid (possibly a bimolecular reduction product). The oily acid, which was obtained in good yield, did not solidify when cooled to −25° and its boiling point did not change on redistillation. It consisted of a mixture of Δ^{β}- and Δ^{γ}-dihydrosorbic acids as shown by oxidation (Found : C, 63·2; H, 8·6. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·8%).

(b) *By sodium amalgam in an acid medium.* To a solution of sorbic acid (25 g.) in excess of glacial acetic acid, 3% sodium amalgam was added in small portions during 7 hours. A large volume of water was added, the mercury separated, and the solution thoroughly extracted with ether. The ethereal solution was washed several times with water, the ether evaporated, and the bulk of the residual

acetic acid distilled at ordinary pressure through a short column. The residue was dissolved in petroleum, freed from unchanged sorbic acid as in (a), and distilled at reduced pressure. An oily acid (b. p. 102—103°/16 mm.) was obtained which did not solidify at —25° and was indistinguishable from the acid mixture obtained in (a). This also was a mixture of Δ^{β}- and Δ^{γ}-dihydrosorbic acids [Found: C, 63·4; H, 8·4; *M* (dibasic), 115. Calc. for $C_6H_{10}O_2$: C, 63·2; H, 8·8%; *M*, 114].

(c) *By aluminium amalgam and sodium sorbate.* Amalgamated aluminium foil was allowed to react with a neutral, aqueous solution of sodium sorbate for 24 hours. The resulting liquor was filtered, acidified, and extracted with ether. Again an oily acid (b. p. 96—98°/12 mm.), indistinguishable from the mixtures of Δ^{β}- and Δ^{γ}-dihydrosorbic acids previously obtained, resulted.

Oxidation of Mixtures of Dihydrosorbic Acids.—Specimens of each of the three mixtures obtained as above were oxidised with 3% permanganate in neutral solution. It was desired to estimate the succinic acid produced and obtain an approximation to the proportion of the Δ^{γ}-acid in the acid mixture.

The acid, suspended in much water, was cooled to 0° and vigorously stirred. An amount of permanganate corresponding to 4 atoms of oxygen per molecule of dihydrosorbic acid was gradually added. The product was worked up in the usual way (the manganese mud being thoroughly extracted with water), and the aqueous liquor concentrated to small bulk on a steam-bath. The product was acidified with the calculated quantity of hydrochloric acid and thoroughly extracted with ether. The mother-liquor was evaporated at room temperature in an evacuated desiccator, and the solid residue repeatedly extracted with acetone. The ethereal extract, evaporated under a long column, yielded a mixture of solid and liquid acids, the acetone extract almost entirely a solid acid. The solid acid from each extract was succinic acid: malonic acid, which should arise from Δ^{β}-dihydrosorbic acid, had been entirely converted into acetic acid. The liquid portion of each oxidation product was distilled: after removal of the low-boiling material, the first fraction was collected up to 120°, the second at 120—135°, and the last few drops of distillate separately; some succinic acid remained in the flask.

A portion of the first fraction was converted into its *p*-bromophenacyl ester (Judefind and Reid, *J. Amer. Chem. Soc.*, 1920, **42**, 1047), which, after recrystallisation until its melting point was constant, was found to be pure *p*-bromophenacyl acetate (m. p. 84°; mixed m. p. with authentic specimen, 84°). The last fraction similarly yielded the *p*-bromophenacyl ester of propionic acid, which

after recrystallisation melted at 57—58° (mixed m. p., 58°). The yields of succinic acid obtained by the three methods of reduction correspond to the following proportions of Δ^{γ}-dihydrosorbic acid in the hydrogenated product: (a) 35%; (b) 40%; (c) 30%.

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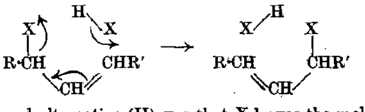
CCXVI.—*Mobile Anion Tautomerism. Part II. A Complementary Study of the Mechanism of Anionotropic Change, with Special Reference to the Fate of the Mobile Anion.*

By HAROLD BURTON.

IN Part I (Burton and Ingold, this vol., p. 904) it was shown that the mobility of the group X in the three-carbon anionotropic system R·CHX·CH:CHR′ ⇌ R·CH:CH·CHXR′ followed the order of the anionic stability of X (*e.g.*, Br > OAc > OH) and the power of R and R′ to supply electrons. Both circumstances suggested that when X leaves the carbon atom to which it is attached it does so as a real or potential anion; *i.e.*, it carries with it the electrons which previously it shared. The precise fate of X, once it has broken from its attachment, was not examined in detail in Part I, but two alternative hypotheses were suggested. The first (I) was that concomitantly with the elimination (ionisation) of X, its equivalent, derived from an assumed catalyst such as HX, may be introduced into the new position by an internal cyclic process:



. . (I.)

The second alternative (II) was that X leaves the molecule as $X^{\ominus}$ in combination with a catalyst (*e.g.*, solvent molecule) to be returned subsequently to the electromeric cation derived from another molecule:

$$\left.\begin{array}{c} \text{R·CHX·CH:CHR}' \rightleftharpoons \text{R·}\overset{\oplus}{\text{C}}\text{H·CH:CHR}' \\ \Updownarrow \\ \text{R·CH:CH·CHXR}' \rightleftharpoons \text{R·CH:CH·}\overset{\oplus}{\text{C}}\text{HR}' \end{array}\right\} + X^{\ominus},\text{(Catalyst)} \quad . \quad \text{(II.)}$$

The type of combination with the catalyst necessary to bring about the removal of X was left undetermined, and the further question therefore arose whether the production of a co-ordinate link is required, or whether the formation of residual electrovalencies arising from attraction due to external molecular fields ("molecular combination," "dipole association," etc.) would suffice. Furthermore, the volatile, non-salt-like character of the anionotropic substances described in Part I indicated that the ionisation of X might not be followed by dissociation of the ions, so that $X^{\ominus}$ might, throughout the isomeric change, remain in electrovalent association with the cation of the molecule which gave rise to it. Thus the possible modifications of mechanism (II) are:

(II*a*) Covalent interaction with catalyst, and ionic dissociation.

(II*b*) Molecular association with catalyst, and ionic dissociation.

(II*c*) Covalent interaction with catalyst; ionisation but no dissociation.

(II*d*) Molecular association with catalyst; ionisation but no dissociation.

A suitable example for detailed study is the conversion of α-phenylallyl *p*-nitrobenzoate into cinnamyl *p*-nitrobenzoate:

$$\underset{\displaystyle Ph\cdot CH\cdot CH{:}CH_2}{\overset{\displaystyle O\cdot CO\cdot C_6H_4\cdot NO_2}{|}} \rightleftharpoons \underset{\displaystyle Ph\cdot CH{:}CH\cdot CH_2}{\overset{\displaystyle O\cdot CO\cdot C_6H_4\cdot NO_2}{|}}$$

The advantages offered by this example are: (1) Both isomerides are crystalline and are easily identified. (2) In three-carbon systems terminated by a single phenyl group the reaction proceeds substantially in one direction and experimental complications arising from a considerable retrograde reaction are avoided (compare Part I). (3) The mobility is of the right order of magnitude for detailed study, interchange occurring at an elevated temperature, and not taking place at an appreciable speed at the ordinary temperature in the presence of any of the reagents or solvents used in this investigation; the equilibrated system, therefore, can be "fixed" by rapid cooling, and disturbances during the isolation of the products obviated.

The main portion of this work has therefore been carried out with the substances mentioned, although experiments with a number of other anionotropic individuals are described. The stages in which the investigation has proceeded are:

(1) α-Phenylallyl *p*-nitrobenzoate was left for some months without change in solution in acetic acid, acetic acid containing a few drops of 30% hydrobromic acid, and alcoholic hydrochloric acid. These observations tell against mechanisms (I), (II*a*), and (II*c*),

for which either a weak or a strong acid ought to furnish the best possible catalyst.

(2) In boiling acetic anhydride α-phenylallyl *p*-nitrobenzoate passes smoothly into its isomeride. This appears to exclude mechanism (I), according to which the products of the change should be cinnamyl acetate and *p*-nitrobenzoic-acetic anhydride. There is, however, one other alternative, namely, that the mixed anhydride might react with cinnamyl acetate, yielding cinnamyl *p*-nitrobenzoate and acetic anhydride.

(3) If this were so, α-phenylallyl alcohol on treatment with an equivalent of the mixed anhydride in acetic anhydride solution should yield only cinnamyl *p*-nitrobenzoate. Actually both cinnamyl acetate and cinnamyl *p*-nitrobenzoate are formed, so mechanism (I) is definitely eliminated.

(4) Final confirmation was obtained by heating cinnamyl acetate with an equivalent of *p*-nitrobenzoic-acetic anhydride under the conditions used in the experiments of sections (2) and (3). No double decomposition occurred.

(5) Carbonyl groups are well known for the facility with which they form co-valency addition compounds with anions, *e.g.*, in the alkaline hydrolyses of esters (*Ann. Reports*, 1927, **24**, 157), and the catalytic activity of acetic anhydride might therefore be due to this cause (hypotheses II*a* and IIc). The dielectric constant of acetic anhydride is 20·5, and the external electrostatic field, as measured by the molecular dipole moment, must be considerable, and might also be the cause of its catalytic activity (hypotheses II*b* and II*d*). Benzonitrile has about the same dielectric constant as acetic anhydride, namely, 26, but chemical evidence shows that the ability of the cyano-group to form covalency addition compounds with anions, if not nil, is at least negligible in comparison with that of carbonyl. Substitution of benzonitrile for acetic anhydride as solvent for the isomerisation showed that conversion occurred equally smoothly and completely. These experiments favour mechanisms II*b* and II*d* and are against II*a* and II*c*.

(6) Unsuccessful attempts were made to find an inert solvent having a dielectric constant of 20 or more, in which covalent union with an anion is structurally impossible. Chlorobenzene fulfils the necessary structural requirements, although its dielectric constant is only 11 (dipole moment $1{\cdot}58 \times 10^{-18}$ E.S.U.). Isomeric change occurred smoothly and substantially completely in this solvent, although definitely more slowly than in the solvents having dielectric constants of about 20. Mechanisms II*a* and II*c* were thus excluded, II*b* or II*d* confirmed.

(7) On either of the latter views it is to be expected that in

p-xylene (dielectric constant 2) the change would proceed with difficulty or not at all, since there are no pre-formed dipoles in this substance, although the anion itself might cause some polarisation. Actually under conditions comparable with those used in (6), a slow and partial isomerisation occurs, together with simultaneous decomposition, the products of which, rather than the xylene, may be responsible for catalysing the interconversion observed.

(8) Finally, decision between mechanisms II*b* and II*d* was obtained by heating α-phenylallyl *p*-nitrobenzoate in acetic anhydride as under (2), except that an equivalent of acetate ions was introduced in the form of tetramethylammonium acetate. If the ionisation and subsequent re-co-ordination of the *p*-nitrobenzoyloxy-group is intramolecular (hypothesis II*d*), the presence of the tetramethylammonium acetate should make no difference to the isomeric change (excepting in so far as it might alter the dielectric constant of the medium); on the other hand, if ionisation is followed by dissociation (hypothesis II*b*), the recombination of the anion with the cation will be inhibited by the competition of the acetate ions, and a large proportion of cinnamyl acetate should be produced. Actually the product was a mixture of cinnamyl acetate and cinnamyl *p*-nitrobenzoate, in which the former preponderated, the ionic dissociation hypothesis thus being confirmed.

Conclusions.—The study of the mechanism of anionotropic change divides itself into two portions:

(1) The behaviour of the electrons in the electromeric cation under different conditions of structure, (2) the behaviour of the eliminated anion under different conditions of catalysis. Aspect (1) was studied in Part I (*loc. cit.*), and as regards aspect (2) it is now shown that the mobile group undergoes ionic dissociation promoted by some molecular property of the solvent closely related to its dielectric constant. It is suggested that the anion combines electrostatically with the catalyst by means of the pre-existing, plus the induced, dipolar field of the latter.

EXPERIMENTAL.

Conversion of α-Phenylallyl p-*Nitrobenzoate into Cinnamyl* p-*Nitrobenzoate.*—A mixture of α-phenylallyl *p*-nitrobenzoate (10 g.) and acetic anhydride (20 c.c.) was boiled for 6 hours and then poured into water. The precipitate (8 g.), m. p. 75° after being washed with water and cold alcohol, gave after one crystallisation from alcohol pure cinnamyl *p*-nitrobenzoate, m. p. and mixed m. p. 77—78°. The alcoholic washings contained a dark oil, but the quantity was too small for examination.

Simultaneous Formation of Cinnamyl Acetate and Cinnamyl p-*Nitrobenzoate from α-Phenylallyl Alcohol.*—A mixture of α-phenylallyl alcohol (4·6 g.), *p*-nitrobenzoyl chloride (6·4 g.), dry sodium acetate (2·82 g.), and acetic anhydride (20 c.c.) was boiled for 6 hours. The mixture was poured into water, and the semi-solid precipitate washed with cold alcohol. The residue (4·85 g.) contained cinnamyl *p*-nitrobenzoate (1·35 g.), which was isolated by washing with dilute sodium hydroxide solution, and the alcoholic washings yielded 3 g. of cinnamyl acetate, b. p. 140°/16 mm., and a further quantity (0·65 g.) of the nitrobenzoate.

When cinnamyl acetate was acted on by a mixture of *p*-nitrobenzoyl chloride and sodium acetate under the above conditions, it was recovered unchanged.

Other Methods of converting α-Phenylallyl p-*Nitrobenzoate into Cinnamyl* p-*Nitrobenzoate.*—(*a*) A solution of the nitrobenzoate (5 g.) in benzonitrile (10 c.c.) was heated at 140° for 6 hours. When the dark solution was poured into an excess of petrol, 0·2 g. of a dark, flocculent precipitate remained undissolved. The filtrate slowly deposited colourless crystals of cinnamyl *p*-nitrobenzoate (1 g.), m. p. 77—78°, and a further quantity (2·5 g.) was obtained by steam distillation of the mother-liquor to remove volatile products, and trituration of the partly solid residue witb alcohol.

(*b*) Solutions of the nitrobenzoate (2·5 g.) in chlorobenzene (5 c.c.) were boiled for 6 and 72 hours, respectively. The cinnamyl derivative was not formed in recognisable amount in the first case, but formed the major part of the product in the second.

(*c*) Experiments (*b*) were repeated with *p*-xylene in place of chlorobenzene. No change was observed after 6 hours, but when reaction took place for 72 hours and the resulting dark brown solution was steam-distilled, a semi-solid residue was obtained. This was dissolved in alcohol, and after 2 days crude cinnamyl *p*-nitrobenzoate (0·85 g.) separated; no definite product could be isolated from the mother-liquor.

α-Phenylallyl *p*-nitrobenzoate decomposes when it is heated at 140° for 6 hours with glycerol or chlorohydrin.

Formation of Cinnamyl Acetate from α-Phenylallyl p-*Nitrobenzoate.*—A mixture of α-phenylallyl *p*-nitrobenzoate (10 g.), tetramethylammonium acetate (4·7 g.), and acetic anhydride (20 c.c.) was boiled for 6 hours. The dark reaction mixture was either (*a*) fractionated, the bath being heated to 200° to ensure that the last trace of cinnamyl acetate was given off (yield of crude acetate, 4 g.; b. p. 134°/10 mm.), or (*b*) poured into warm water, and the precipitated *p*-nitrobenzoic acid separated and washed with ether. The ethereal washings together with the ethereal extract of the aqueous filtrate yielded

on evaporation a further quantity of the acid; total, 3·5 g. The residue on distillation gave 4·0 g. of cinnamyl acetate, b. p. 134°/10 mm., leaving 2·5 g. of crude cinnamyl *p*-nitrobenzoate in the flask.

Further examples of transformations similar to those recorded on p. 1653 are the production of *p*-chlorocinnamyl *p*-nitrobenzoate and 3-*methylcinnamyl* *p-nitrobenzoate* from α-*p*-chlorophenylallyl *p*-nitrobenzoate and α-*m*-tolylallyl *p*-nitrobenzoate, respectively.

Attempted Transformations in Other Solvents.—A solution of α-phenylallyl alcohol or its *p*-nitrobenzoate in chloral (compare Part I, p. 909) was heated at 65° for 6 hours, and a solution of α-phenylallyl alcohol in benzonitrile was treated as described on p. 1654. In no case was isomerisation into the cinnamyl derivative noticed.

α-p-*Chlorophenylallyl Alcohol*, $C_6H_4Cl{\cdot}CH(OH){\cdot}CH{:}CH_2$.—The Grignard reagent prepared from magnesium (6 g.), *p*-chloroiodobenzene (60 g.), ether (100 c.c.), and a trace of iodine was cooled below 0° and treated during 1 hour with a solution of acraldehyde (14 g.) in ether (72 c.c.). The mixture was well stirred for a further 3 hours and then decomposed by ice and dilute hydrochloric acid. The oil obtained after extraction with ether, washing with sodium bicarbonate solution, drying, and evaporation was distilled, and a fraction (20 g.), b. p. 125—128°/12 mm., collected. The *alcohol* boils at 122—123°/10 mm. (Found: Cl, 21·4. C_9H_9OCl requires Cl, 21·05%). The high value for chlorine is probably due to a small amount of impurity (see below) which cannot be eliminated by repeated distillation. The p-*nitrobenzoate* was prepared as described for the phenylallyl analogue (Burton and Ingold, *loc. cit.*), but it was necessary to crystallise the crude product five times from methyl alcohol, colourless, glistening plates, m. p. 81—82°, being formed (Found: C, 60·5; H, 3·9. $C_{16}H_{12}O_4NCl$ requires C, 60·45; H, 3·8%), and when the mother-liquors were partly evaporated in a vacuum a small quantity of a substance was obtained which separated from ethyl alcohol in long, silky needles, m. p. 170° after previous softening (Found: C, 56·5, 56·5; H, 3·4, 3·3%).

Conversion of α-p-*Chlorophenylallyl Alcohol into* p-*Chlorocinnamyl Alcohol.*—A mixture of α-*p*-chlorophenylallyl alcohol (11·5 g.) and acetic anhydride (12 c.c.) was boiled for 6 hours and then distilled, 3·7 g. of the unchanged alcohol and 8 g. of an *acetate*, b. p. about 155°/11 mm., being obtained. The latter, on hydrolysis with 5% alcoholic potassium hydroxide (200 g.) for 3 hours, yielded p-*chlorocinnamyl alcohol*, which crystallised from ligroin (b. p. 40—60°) in clusters of long, colourless needles, m. p. 57—58° (Found: C, 64·2; H, 5·55. C_9H_9OCl requires C, 64·1; H, 5·4%). The p-*nitrobenzoate*, prepared by the pyridine method, crystallised from alcohol in

almost colourless, prismatic needles, m. p. 130—131° (Found: C, 60·5; H, 3·9. $C_{16}H_{12}O_4NCl$ requires C, 60·45; H, 3·8%).

Bromide from α-p-Chlorophenylallyl Alcohol (*p-Chlorocinnamyl Bromide*, $C_6H_4Cl·CH\colon CH·CH_2Br$).—To the alcohol (8·4 g.), cooled in ice, a cold solution of hydrogen bromide in glacial acetic acid (30%; 50 g.) was added gradually. After solution occurred, a colourless, crystalline mass separated, which was poured into water, collected, washed free from acetic acid, and dried (yield 10 g.). The *bromide* dissolves readily in hot glacial acetic acid and separates, on cooling, in colourless plates, m. p. 62—63° (Found: 0·1910 gave 0·2732 AgCl + AgBr. C_9H_8ClBr requires AgCl + AgBr = 0·2732). The same bromide was obtained from *p*-chlorocinnamyl alcohol. Ozonolysis of a chloroform solution of the bromide (see Burton and Ingold, *loc. cit.*) gave *p*-chlorobenzoic acid and bromoacetaldehyde.

α-m-Tolylallyl Alcohol, $C_6H_4Me·CH(OH)·CH\colon CH_2$.—The Grignard reagent prepared from magnesium (12 g.), *m*-iodotoluene (109 g.), ether (250 c.c.), and a trace of iodine was treated with a solution of acraldehyde (28 g.) in ether (100 c.c.) as described for the chloro-compound. The gummy reaction product was decomposed with ice and dilute acetic acid, and the oil obtained fractionated. The *alcohol* boils at 115—117°/11 mm., and is a colourless mobile oil (yield, 30%). The p-*nitrobenzoate*, prepared by the pyridine method, crystallised from alcohol in almost colourless, glistening plates, m. p. 53° (Found: C, 68·75; H, 4·7. $C_{17}H_{15}O_4N$ requires C, 68·7; H, 5·1%).

α-3-Methylcinnamyl Alcohol, $C_6H_4Me·CH\colon CH·CH_2·OH$.—The transformation of *α-m*-tolylallyl alcohol into 3-methylcinnamyl acetate, b. p. about 145°/13 mm., was complete after 6 hours' boiling with acetic anhydride. Hydrolysis of the acetate furnished 3-*methylcinnamyl alcohol*, b. p. 137—140°/11 mm., as a colourless, mobile oil, which could not be induced to solidify. The p-*nitrobenzoate* separated from alcohol in almost colourless, prismatic needles, m. p. 63—64° (Found: C, 68·5; H, 4·8. $C_{17}H_{15}O_4N$ requires C, 68·7; H, 5·1%).

Bromide from α-m-Tolylallyl Alcohol.—The bromide was prepared, in a similar manner to the corresponding *p*-chloro-compound, from the tolylallyl alcohol (7·5 g.) and an acetic acid solution of hydrobromic acid (30%; 50 g.); after 15 minutes, the dark solution was poured into water. The *bromide*, extracted with ether and washed free from acids by sodium bicarbonate solution, was a straw-coloured oil, b. p. 138—140°/11 mm. (with slight decomp.), which slowly decomposed into a black, viscous mass. Ozonolysis of a chloroform solution of a freshly prepared specimen, and subsequent decomposition of the oily ozonide with boiling water, gave mainly *m*-toluic

acid and bromoacetaldehyde, together with a small quantity of a volatile aldehyde (formaldehyde ?).

The author wishes to express his thanks to Professor C. K. Ingold, D.Sc., F.R.S., for his valued advice and criticism, and to the Government Grant Committee of the Royal Society for a grant which has helped to defray the cost of this investigation.

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CCXVII.—*αγ-Diamino-β-phenylpropane and Related Compounds of Pharmacological Interest.*

By JOSEPH GILBERT JACKSON and JAMES KENNER.

BOTH ethylenediamine and αε-diaminopentane are characterised pharmacologically by a depressant action on the blood pressure (Cloetta and Wünsche, *Arch. exp. Path. Pharm.*, 1923, **96**, 307; Barger and Dale, *J. Physiol.*, 1920, **41**, 19), and although the behaviour of other polymethylenediamines in this respect does not appear to have been recorded, it may be anticipated that they would exert a similar effect. This is in interesting contrast with the well-known sympathomimetic or pressor influence of β-phenylethylamine and related compounds (Barger and Dale, *loc. cit.*). It therefore seemed worthy of inquiry whether *αγ-diamino-β-phenylpropane*, $CHPh(CH_2{\cdot}NH_2)_2$, would behave as an intensified β-phenylethylamine, or whether its relationship to αγ-triaminopropane would involve more or less complete suppression of any sympathomimetic action.

The base and its NN′-*dimethyl* derivative have therefore been prepared by applying the usual series of reactions to β-*phenylglutardihydrazide*, $CHPh(CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2)_2$, and kindly examined by Dr. S. J. Cowell in the laboratory of Professor E. Mellanby, F.R.S. They were found to produce no appreciable effect upon the blood pressure of a cat, and, further, although Barger and Dale (*loc. cit.*) found that the introduction of hydroxyl groups in the 4- or 3 : 4-positions intensifies the activity of β-phenylethylamine, the hydrobromides of *αγ-diamino-β-4-hydroxyphenylpropane* and of *αγ-diamino-β-3 : 4-dihydroxyphenylpropane* are also reported by Dr. J. H. Burn to be devoid of all but traces of a sympathomimetic action.

The stereochemical considerations previously discussed (Jackson and Kenner, this vol., p. 573) suggest that the intramolecular condensation of diacyl derivatives of αγ-diamino-β-phenylpropane will

only result in the formation of one dihydro*iso*quinoline ring, and this was confirmed by experiment.

*4-Aminomethyl-1-methyl-3 : 4-dihydro*iso*quinoline*,

$$C_6H_4<\begin{matrix}CH(CH_2\cdot NH_2)\cdot CH_2\\ CMe=\!=\!=\!=\!=\!=\!=N\end{matrix},$$

and the corresponding 1-*phenyl* derivative, thus obtained, may also be considered as compounds in which elements favouring pressor and depressor actions respectively are combined, since, for example, 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline hydrochloride (Pyman, J., 1908, **95**, 1743), as well as hydrastinine and cotarnine, exerts a depressant action. In the new compounds, however, the two effects are not as nicely balanced as in $\alpha\gamma$-diamino-β-phenylpropane, since, as Dr. Cowell found, administration of each compound causes definite depression of the blood pressure of a cat.

EXPERIMENTAL.

Ethyl β-*phenylglutarate* is a colourless viscous oil, b. p. 180—184°/14 mm. (Found : C, 68·3 ; H, 7·5. $C_{15}H_{20}O_4$ requires C, 68·2 ; H, 7·6%).

β-*Phenylglutardihydrazide*, prepared from the ester, crystallises from absolute alcohol in long prisms, m. p. 177°, easily soluble in water (Found : N, 24·0. $C_{11}H_{16}O_2N_4$ requires N, 23·8%).

In order to obtain the corresponding *urethane*, amyl nitrite (15 g.) was added to a solution of the dihydrazide (9 g.) in absolute alcohol (500 c.c.) which had been cooled to 25° before treatment with a solution of dry hydrogen chloride (3 g.) in absolute alcohol. After the mixture had been heated until the evolution of nitrogen was complete, the solvent was removed by the aid of steam. By extraction with benzene, the urethane was obtained as a brown syrup (11 g.), from which crystals slowly separated. By crystallisation from benzene–light petroleum, long, colourless needles, m. p. 73—74°, insoluble in water and ligroin, were obtained (Found : N, 9·7. $C_{15}H_{12}O_4N_2$ requires N, 9·5%).

The urethane syrup (70 g.) was boiled with hydrobromic acid (b. p. 125° ; 700 c.c.) for 6 hours, and the major portion of the acid was then removed from the hot filtered solution by distillation. β-Phenylglutaric acid (10 g.) was recovered from the residual liquor by extraction with ether. Evaporation of the aqueous solution to a syrupy consistency furnished $\alpha\gamma$-*diamino*-β-*phenylpropane hydrobromide* (32 g.), which separated from alcohol–ether in colourless prisms, melting at 252° and decomposing at 272° (Found : Br, 51·3. $C_9H_{14}N_2$,2HBr requires Br, 51·3%). The free *base*, b. p. 150°/15 mm., is miscible with water in all proportions, giving an alkaline solution, and is rapidly converted in the atmosphere into its car-

bonate, m. p. 172° (decomp.). The *picrate* separates from alcohol in yellow prisms, m. p. 247° (decomp.) (Found : N, 19·0. $C_{21}H_{20}O_{14}N_8$ requires N, 18·5%). The *diacetyl* derivative crystallises from benzene in stout prisms, m. p. 153—154°, easily soluble in water, alcohol and hot benzene (Found : N, 12·1. $C_{13}H_{18}O_2N_2$ requires N, 12·0%). The *dibenzoyl* derivative separates from alcohol in colourless needles, m. p. 179°, easily soluble in alcohol, but very sparingly soluble in water (Found : N, 7·9. $C_{23}H_{22}O_2N_2$ requires N, 7·8%). The pp'-*ditoluenesulphonyl* derivative crystallises from alcohol in slender prisms, m. p. 91° (Found : N, 6·2. $C_{23}H_{26}O_4N_2S_2$ requires N, 6·1 %), and was easily converted by means of methyl sulphate into NN'-*dimethyl*-NN'-*di*-p-*toluenesulphonyl*-αγ-*diamino*-β-*phenylpropane*, m. p. 60°, which could not be crystallised and was therefore purified by pouring its solution in cold concentrated sulphuric acid into water (Found : N, 5·7. $C_{25}H_{30}O_4N_2S_2$ requires N, 5·8%). Hydrolysis occurred when a solution of the methyl derivative (5 g.) in sulphuric acid (20 c.c.) and glacial acetic acid (10 c.c.) was maintained at 100° for 8 hours. The mixture was then made strongly alkaline, and the base removed in steam. From the distillate, NN'-*dimethyl*-αγ-*diamino*-β-*phenylpropane hydrochloride* was prepared in the usual manner; it crystallised from alcohol–ether in prisms, m. p. 249° (Found : Cl, 28·1. $C_{11}H_{18}N_2$,2HCl requires Cl, 28·2%).

γ-*Amino*-β-*phenylbutyric acid hydrobromide*, isolated when the filtrate from the preparation of phenyldiaminopropane hydrobromide was evaporated, separated from benzene in colourless, irregular plates, m. p. 114° (Found : N, 5·5. $C_{10}H_{13}O_2N$,HBr requires N, 5·4%). On treatment with cold 10% aqueous potassium hydroxide solution, 4-*phenyl*-2-*pyrrolidone* was obtained, which crystallised from benzene–light petroleum in colourless, hexagonal prisms, m. p. 60° (Found : N, 8·9. $C_{10}H_{11}ON$ requires N, 8·7%). Its *acetyl* derivative separated from alcohol in hexagonal plates, m. p. 63° (Found : C, 70·5, 70·8; H, 6·8, 7·2; N, 7·4, 7·6. $C_{12}H_{13}O_2N$ requires C, 71·0; H, 6·4; N, 6·9%). The *benzoyl* derivative crystallised from benzene–light petroleum in colourless prisms, m. p. 145° (Found : C, 76·7, 77·2; H, 5·6, 5·4; N, 5·3. $C_{17}H_{15}O_2$ requires C, 77·0; H, 5·7; N, 5·3%).

4-*Aminomethyl*-1-*methyl*-3 : 4-*dihydro*iso*quinoline* resulted when a solution of diacetylphenyldiaminopropane (5 g.) in toluene (150 c.c.) was boiled with phosphoric oxide (30 g.) for 12 hours, and for a further 8 hours after addition of more pentoxide (5 g.). The decanted solution was treated with water, toluene removed in steam, and the residue rendered alkaline; the *base* (1·5 g.) then separated. It crystallised from benzene in colourless, hexagonal plates, m. p.

182°, easily soluble in alcohol and dilute acids (Found: C, 75·6; H, 8·4; N, 16·0. $C_{11}H_{14}N_2$ requires C, 75·8; H, 8·0; N, 16·1%), and its *hydrochloride* separated from a mixture of alcohol and ether in slender prisms, m. p. 222°, very soluble in water.

*4-Aminomethyl-1-phenyl-3 : 4-dihydro*iso*quinoline.*—The benzoyl derivative (7 g.) of this base was obtained by boiling a solution of dibenzoylphenyldiaminopropane (10 g.) in toluene (500 c.c.) with phosphoric oxide (40 g.) for 26 hours, and separated when the acid solution of the reaction products was almost neutralised. The free *base* (0·1 g.) and unchanged dibenzoyl derivative (0·2 g.) were recovered when the liquors were rendered alkaline. The *benzoyl* derivative crystallised from alcohol in long prisms, m. p. 114° (Found: N, 8·5. $C_{25}H_{20}ON_2$ requires N, 8·2%), and was converted, by boiling 50% sulphuric acid, into the free base. This separated from aqueous alcohol in colourless leaflets, m. p. 169° (Found: C, 81·6; H, 7·1; N, 12·1. $C_{16}H_{16}N_2$ requires C, 81·4; H, 6·8; N, 11·8%). Its *dihydrochloride* formed colourless prisms, m. p. 291°.

Ethyl p-*methoxyphenylpropane-ααγ-tricarboxylate* was produced when ethyl malonate (214 g.) and ethyl *p*-methoxycinnamate (280 g.) were mixed with a solution of sodium (30 g.) in absolute alcohol (500 g.), the whole being kept at the ordinary temperature for 14 days. The ester (275 g.) was a yellow, viscous oil, b. p. 225—240°/12 mm. (Found: C, 62·5; H, 7·0. $C_{19}H_{26}O_7$ requires C, 62·4; H, 7·1%). Hydrolysis readily ensued when the ester (60 g.) was mixed with a solution of sodium hydroxide (40 g.) in water (50 c.c.) and alcohol (21 c.c.). After the reaction had subsided, and the product had been dissolved in water (200 c.c.), methoxycinnamic acid (3 g.) was precipitated by partial acidification. After concentration of the solution to 100 c.c., and further acidification, the crude tricarboxylic acid was removed by ether and converted at 130° into the dicarboxylic acid. After crystallisation from hot water, β-p-*methoxyphenylglutaric acid* (35 g.) was obtained in colourless prisms, m. p. 165° (Found: C, 60·6; H, 6·2; equiv., 121·5. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%; equiv., 119). It was characterised by its *anhydride*, slender prisms, m. p. 152° (Found: C, 65·2; H, 5·6. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%), its *methyl* ester, slender prisms, m. p. 42°, b. p. 205—210°/20 mm. (Found: C, 63·1; H, 6·6. $C_{14}H_{18}O_5$ requires C, 63·2; H, 6·8%), its *ethyl* ester, b. p. 206—210°/14 mm. (Found: C, 64·9; H, 7·5. $C_{16}H_{22}O_5$ requires C, 65·3; H, 7·5%), and its *dihydrazide*, needles, m. p. 190° (Found: C, 54·2; H, 6·8. $C_{12}H_{18}O_3N_4$ requires C, 54·2; H, 6·8%). The corresponding *diurethane* separated from aqueous alcohol in slender prisms, m. p. 99—100° (Found: C, 59·2; H, 7·8. $C_{16}H_{24}O_5N_2$

requires C, 59·3; H, 7·4%). Hydrolysis with boiling hydrobromic acid (*d* 1·45) was accompanied by demethylation.

αγ-Diamino-β-p-hydroxyphenylpropane dihydrobromide crystallised from alcohol–ether in irregular prisms, m. p. 316°, easily soluble in water and furnishing a violet coloration with ferric chloride (Found: Br, 49·3. $C_9H_{14}ON_2,2HBr$ requires Br, 48·8%). The *tribenzoyl* derivative crystallised from alcohol in nodules of irregular prisms, m. p. 206—207° (Found: C, 75·0; H, 5·6. $C_{30}H_{26}O_4N_2$ requires C, 75·2; H, 5·4%).

3 : 4-*Dimethoxybenzylidenemalonic acid* (3·5 g.) resulted with 3 : 4-dimethoxycinnamic acid (10 g.) when veratraldehyde (15 g.), malonic acid (15 g.), and alcoholic ammonia (4*N*, 50 c.c.) were heated at 100° for 6 hours. The acid crystallised from water in light yellow prisms, m. p. 208° (decomp.) (Found: C, 57·3; H, 4·9. $C_{12}H_{12}O_6$ requires C, 57·2; H, 4·8%).

Ethyl β-3 : 4-*dimethoxyphenylpropane-ααγ-tricarboxylate* was prepared in a similar manner to the monomethoxy-derivative. The reaction mixture set almost solid, but after 14 days the crude product, b. p. 225—250°/16 mm., consisted to the extent of only 84% of the desired ester. This after further fractionation boiled at 245—248°/14 mm., was very viscous, and exhibited a faint green fluorescence (Found: C, 60·4; H, 7·2. $C_{20}H_{28}O_8$ requires C, 60·6; H, 7·1%). Alkaline hydrolysis, as in the previous case, was almost instantaneous, and dimethoxycinnamic acid was removed by rendering the solution of the crude sodium salt just acid.

3 : 3′-*Dimethoxydiphenylglutaric acid* separated from water in colourless prisms, which melted in the hydrated condition (Found: H_2O, 6·3. $C_{13}H_{16}O_6,H_2O$ requires H_2O, 6·3%) at 125—130°, and when anhydrous at 184° (Found: C, 58·6; H, 6·1. $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0%). It was characterised by its *anhydride*, hexagonal prisms, m. p. 124° (Found: C, 62·4; H, 5·6. $C_{13}H_{14}O_5$ requires C, 62·4; H, 5·6%), its *methyl* ester, needles, m. p. 73° (Found: C, 61·0; H, 6·9. $C_{15}H_{20}O_6$ requires C, 60·8; H, 6·8%), its *ethyl* ester, b. p. 226—229°/15 mm. (Found: C, 62·7; H, 7·5. $C_{17}H_{24}O_6$ requires C, 63·0; H, 7·4%), and its *dihydrazide*, needles, m. p. 182° (Found: C, 53·1; H, 6·8. $C_{13}H_{20}O_4N_4$ requires C, 52·7; H, 6·8%). The syrupy urethane prepared from the last compound could not be obtained in the solid condition, and was therefore directly hydrolysed in 24 hours by boiling hydrobromic acid (*d* 1·45). Dealkylation also occurred and *αγ-diamino-*β-3 : 4-*dihydroxyphenylpropane dihydrobromide* was obtained in stout, hydrated prisms (Found: H_2O, 5·2. $C_9H_{14}O_2N_2,2HBr,H_2O$ requires H_2O, 5·0%). In the anhydrous condition, the salt melted at 294° (Found: N, 8·0; Br, 46·4. $C_9H_{14}O_2N_2,2HBr$ requires N, 8·1;

Br, 46·6%). The *tetrabenzoyl* derivative separated from alcohol in small prisms, m. p. 217° (Found: C, 74·5; H, 5·1; N, 5·1. $C_{27}H_{30}O_6N_2$ requires C, 74·3; H, 5·0; N, 5·9%).

The authors are pleased to record their thanks to the gentlemen named in the text for their co-operation in testing the pharmacological behaviour of the compounds submitted to them.

One of the authors (J. G. J.) makes grateful acknowledgment of assistance by a maintenance grant from the Department of Scientific and Industrial Research, which enabled him to participate in this work. Their thanks are also due to the Research Fund Committee of the Chemical Society for a grant towards the expenses of this work.

THE UNIVERSITY, SHEFFIELD. [*Received, April 28th*, 1928.]

CCXVIII.—*Mobile Hydrogen Tautomerism analogous to the Wagner–Meerwein Re-arrangement. Part II. The Tautomerism of* 1 (*or* 5)-*Hydroxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentan*-5 (*or* 1)-*one and its Derivatives.*

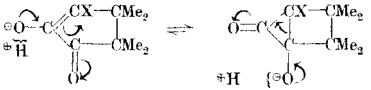
By CHARLES WILLIAM SHOPPEE.

THE two methods of electron redistribution ("inductive" and "electromeric") which have been considered in recent communications from these laboratories are characterised by the circumstance that the displaced duplets are assumed to be retained in the same octet ($\longrightarrow C, \overset{\frown}{—C}$), but in Part I of this series (this vol., p. 365) a general formula was given for changes such as the Wagner–Meerwein, pinacol–pinacolin, semi-pinacolic deamination, and benzil–benzilic acid, in which a duplet was assumed to pass over completely from one octet to an adjacent octet ($\overset{\frown}{C—C}$):

$$\mathrm{X} \overset{\frown}{-} a - \overset{\overset{\mathrm{R}}{|}}{b} - c \overset{\frown}{-} y \longrightarrow \mathrm{X}^{\oplus} + a = b - \overset{\overset{\mathrm{R}}{|}}{c} + y^{\ominus}.$$

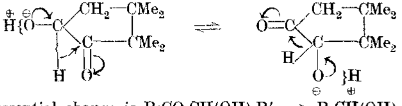
This third method of electron-redistribution may be called the "pinacolic" displacement.

In the examples of tautomerism depending on the process studied in Part I, the bonds b–R and c–R were carbon–carbon bonds, so that the duplet displaced from the octet of b to that of c was still retained in the octet of R:



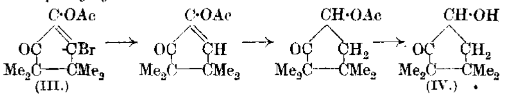
It therefore became of interest to endeavour to determine whether the octet of R was a necessary factor in the situation, and accordingly this paper reports the results of the examination of a case in which R is hydrogen.

An opportunity to test the matter arose through the preparation of the *hydroxy-ketone* named in the title. It was crystalline (m. p. 142°) and exhibited the physical behaviour of a pure substance, but, according to the foregoing hypothesis, might nevertheless exhibit tautomerism of the following kind :

(I.)  (II.)

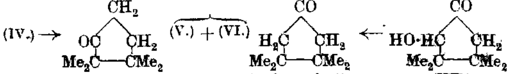
The essential change is R·CO·CH(OH)·R′ ⇌ R·CH(OH)·COR′, and for reasons now to be given is regarded as proceeding by the mechanism formulated above. Some possible alternative suggestions are considered in the sequel.

The substance was prepared from the crystalline acetoxybromo-compound (III) (Part I) in the stages represented below, and according to its method of formation should therefore have formula (IV). The presence of hydroxyl and carbonyl groups was diagnosed by the preparation of a crystalline p-*nitrobenzoyl* derivative and a p-*nitrophenylhydrazone*.



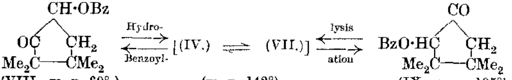
(III.) (IV.)

Further examination quickly revealed its dual chemical character. On treatment with acid reducing agents a mixture of isomeric tetramethyl*cyclo*pentanones (V and VI) was produced, the main isomeride in which is more easily represented as a reduction product of (VII); the ketone similarly derived from (IV) was present in small quantity only :



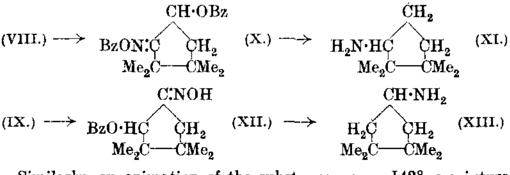
(by-product) (main product) (VII.)

Confirmation of the view that forms (IV) and (VII) attain equilibrium in solution was forthcoming during attempts to locate the positions in which acylation and oximation occur. For the former purpose the hydroxy-ketone (m. p. 142°) was benzoylated with excess of benzoyl chloride in pyridine solution. The product was a mixture separable into two isomerides (m. p.'s 60° and 105°), to which formulæ (VIII) and (IX) have been assigned for reasons which will be given.



(VIII., m. p. 60°.) (m. p. 142°) (IX., m. p. 105°)

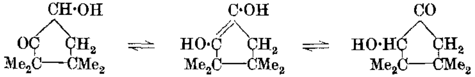
In the first place, both benzoyl derivatives on hydrolysis yield the same parent hydroxy-ketone, m. p. 142°. Secondly, the *benzoyl* derivative, m. p. 60°, on conversion into an *oxime* and complete reduction of the *benzoyl* derivative (X) of the latter, gave 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine (XI) (compare Part I), whereas the isomeric *benzoyl* derivative, m. p. 105°, yielded an *oxime* (XII) which, when fully reduced, gave 3 : 3 : 4 : 4-tetramethyl*cyclo*pentylamine (XIII) (*loc. cit.*). Thirdly, whereas the benzoyl compound, m. p. 60°, is unaffected by bromine in chloroform or acetic acid, the isomeride, m. p. 105°, is readily brominated in chloroform solution, giving a bromination product which is under investigation. It is, of course, normal that the benzoyloxy-group should inhibit bromination on the adjacent carbon atom, whereas the carbonyl group would promote that process.



Similarly, on oximation of the substance, m. p. 142°, a mixture of oximes was obtained. They could not be separated, but the presence of both types was proved by reduction to a mixture of 2 : 2 : 3 : 3- and 3 : 3 : 4 : 4-tetramethyl*cyclo*pentylamines. Other substitution products of the parent hydroxy-ketone are described in the experimental portion.

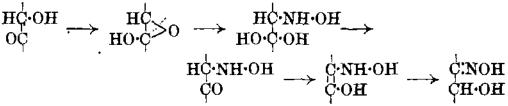
In addition to the hypothesis mentioned at the commencement of this paper, there are two other mechanisms which might be advanced

to account for the tautomerism of the substance of m. p. 142°. First, a succession of triad changes might be suggested :

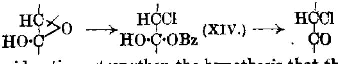


This is an *intrinsically unsatisfactory hypothesis* (except possibly in its application to catalysis by strong alkalis), because the hydroxyl group would work against the enolisation of the adjacent ·CH·CO group ; but in any event, it is regarded as excluded by the fact that the change of structure is manifested by acylation under conditions in which the intermediate diol would be expected to appear as its diacyl derivative, further change being thus arrested. The experiment corresponds, indeed, to that whereby Thiele showed that 1 : 4-addition occurs in the reduction of benzil by reducing it in the presence of acetic anhydride and isolating diacetoxystilbene.

The second suggestion is one which has been made recently by v. Auwers and Mauss (*Biochem. Z.*, 1928, **192**, 200), whose observations on the reactions of unsymmetrical α-ketols (see also Favorski, *Bull. Soc. chim.*, 1926, **39**, 216) are evidently related to those described in this paper. Their mechanism involves keto-cyclol tautomerism with the production of an ethylene oxide, followed by fission of the oxide ring in a different direction, and then a succession of triad changes. Thus, for oximation, the process is written :

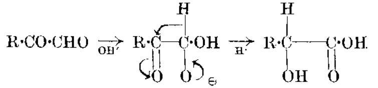


The intrinsic improbability of this is very great indeed, for the postulated ethylene oxide is not an ordinary ethylene oxide but an internal acetal of a type of which no known example exists; moreover, if it were formed, it would certainly not split in the direction suggested. Furthermore, the application of the suggestion to explain benzoylation leads to the intermediate (XIV) which, if formed, would at once yield a chloro-ketone without a change of type, not a benzoyloxy-ketone with one :



These considerations strengthen the hypothesis that the pinacolic displacement can occur with the duplet of a hydrogen atom, and as

an application it may be suggested that the general reaction whereby α-keto-aldehydes yield glycollic acid derivatives in the presence of alkalis is of this type:



It is not impossible that the sugar transformations, typified by (glucose, mannose) ⇌ fructose, which again take place in the presence of alkalis, also involve the pinacolic displacement, although in this case further evidence is naturally desirable.*

Experimental.

1 (*or* 5)-*Hydroxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentan*-5 (*or* 1)-*one* (I or II).—A boiling solution of bromoacetoxyphorone (22 g.) in glacial acetic acid was treated with 35 g. of zinc dust during 6 hours. The cooled solution was filtered, the solid residue washed by decantation with fresh acetic acid, and the combined filtrates thrown into water and extracted with ether. The extract was thoroughly washed with ice-cold 5% sodium hydroxide solution, dried, evaporated, and distilled in a vacuum. A small first fraction, consisting of 5-acetoxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone, b. p. 114°/10 mm., was followed by the main fraction, b. p. 120—121°/10 mm., which consisted of 5-acetoxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentanone (11 g.). This, on hydrolysis on the steam-bath for ½ hour with aqueous-alcoholic sodium hydroxide yielded a clear pale yellow solution, from which, after addition of water, ether extracted the *hydroxy-ketone* (5—6 g.), which was obtained as a white crystalline solid, m. p. 142° (Found: C, 69·2; H, 10·0. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%).

The substance closely resembles the unsaturated hydroxy-ketone (Part I) in odour, volatility, and solubility; it is extremely soluble in all organic solvents, but can be recrystallised with difficulty from ice-cold ligroin (b. p. 30—40°). It is remarkably stable to neutral permanganate in aqueous acetone solution, and but slowly oxidised by alkaline permanganate. It reduces Fehling's solution with great ease, reduction proceeding at 30°; it gives no colour with aqueous-alcoholic ferric chloride solution.

The p-*nitrophenylhydrazone* was prepared by heating a solution of *p*-nitrophenylhydrazine hydrochloride in aqueous sodium acetate with the hydroxy-ketone for a short time. It separated from alcohol

* For another probable application, see Burton and Ingold (this vol., p. 908).

in golden-yellow needles, m. p. 223—224° (decomp.) (Found : C, 62·0; H, 7·0. $C_{15}H_{21}O_3N_3$ requires C, 61·85; H, 7·2%).

The p-*nitrobenzoyl* derivative was obtained by treating the hydroxy-ketone with *p*-nitrobenzoyl chloride in pyridine solution, and crystallised from dilute alcohol in colourless needles, m. p. 85° (Found : C, 62·5; H, 6·4. $C_{16}H_{19}O_5N$ requires C, 62·9; H, 6·3%).

*Reduction of the Hydroxy-ketone to 2 : 2 : 3 : 3-Tetramethyl*cyclo*pentanone and 3 : 3 : 4 : 4-Tetramethyl*cyclo*pentanone*.—(1) *With hydriodic acid*. The hydroxy-ketone (0·6 g.) was heated with 10 c.c. of hydriodic acid (*d* 1·7) in a bath at 130—140° for ½ hour, a slow stream of carbon dioxide being passed to assist sublimation of the ketones. The sublimate was dissolved in a little alcohol and treated with semicarbazide acetate (see below).

(2) *With zinc and hydrochloric acid*. The hydroxy-ketone (0·5 g.) was reduced under reflux for ½ hour, and the sublimate which formed was then washed into semicarbazide acetate solution with a little alcohol.

In both cases rapid formation of 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanonesemicarbazone took place (5 mins.), and after ½ hour the solutions were diluted and filtered. Both products, on crystallisation from alcohol, separated in the characteristic form (pearly plates) and melted at 224° (decomp.); neither product depressed the melting point of a genuine specimen. The filtrates each deposited after 48 hours a small amount of a crystalline semicarbazone. Both specimens, on crystallisation from dilute methyl alcohol, separated as colourless needles, and were identified as 2 : 2 : 3 : 3-tetramethyl*cyclo*pentanonesemicarbazone by direct comparison and by the method of mixed melting points.

*Benzoylation of the Hydroxy-ketone, m. p. 142° : Formation of 5-Benzoyloxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentan-1-one and 1-Benzoyloxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentan-5-one*.—The hydroxy-ketone (2·5 g.) was treated with 5 c.c. of benzoyl chloride in dry pyridine solution for 1 hour on the steam-bath. The product was poured into water and extracted with ether, and the ethereal extract washed thrice with dilute hydrochloric acid, twice with cold 5% sodium hydroxide solution, and finally with water. After drying with calcium chloride, evaporation, and evacuation the oil obtained soon crystallised.

Recrystallisation from dilute methyl alcohol yielded two fractions: (A) m. p. 85—88°, colourless needles, constituting the bulk of the product (2·0 g.), and (B) m. p. 48—50°, colourless plates (0·6 g.). (A) after two recrystallisations from ligroin (b. p. 60—80°) had m. p. 105°, unchanged by further crystallisation, and (B), twice crystallised from ligroin (b. p. 40—60°), had a constant melting point of 60°.

1-*Benzoyloxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentan*-5-*one* (IX) crystallises well from methyl alcohol or from ligroin (b. p. 60—80°) in needles, m. p. 105°, and a mixture with the isomeride, m. p. 60°, had m. p. 52° (Found : C, 73·5 ; H, 7·8. $C_{16}H_{20}O_3$ requires C, 73·8 ; H, 7·7%). It reduces Fehling's solution, probably owing to hyrolysis to the hydroxy-ketone.

Treatment with aqueous-alcoholic sodium hydroxide at 100° for ½ hour yielded the parent hydroxy-ketone, m. p. 141—142°, mixed m. p. 142°, and identity was confirmed by preparation of the *p*-nitrophenylhydrazone, m. p. and mixed m. p. 223—224°.

A single crystalline *oxime* was formed by the action of hydroxylamine acetate in boiling absolute alcohol. After 2 hours the product from 1·1 g. of the derivative, 0·3 g. of hydroxylamine hydrochloride, and 0·4 g. of anhydrous sodium acetate was poured into water and extracted with ether : from the extract, a thick oil was obtained which crystallised on being rubbed with ligroin and then separated from ligroin (b. p. 60—80°) in colourless prisms, m. p. 115° (yield, 1 g.) (Found : C, 69·6 ; H, 8·0. $C_{16}H_{21}O_3N$ requires C, 69·8 ; H, 7·7%). The oxime gave no colour with ferric chloride, and reduced Fehling's solution on boiling. On treatment with benzoyl chloride in dry pyridine solution, it yielded a *benzoyl-oximino*-derivative, which after two crystallisations from ligroin (b. p. 80—100°) formed stellate clusters of prisms, m. p. 135° (Found : C, 72·9 ; H, 6·75. $C_{23}H_{25}O_4N$ requires C, 72·8 ; H, 6·6%).

Reduction of the oxime (*m. p.* 115°). The oxime (0·7 g.), dissolved in a little alcohol at 60°, was reduced with 50 g. of 2·5% sodium amalgam with the continuous addition of glacial acetic acid. The product was diluted with water and extracted with ether twice ; the aqueous solution was basified and extracted with ether, and the ethereal extract dried with anhydrous potassium carbonate and evaporated under a column. The resulting 3 : 3 : 4 : 4-tetramethyl*cyclo*pentylamine crystallised readily, and after being washed with cold ligroin had m. p. 100°, mixed m. p. 100—101° with a genuine specimen. The picrate, prepared in alcoholic solution, had m. p. 250—252° (decomp.), and its identity was established by direct comparison and mixed melting point. The acetyl derivative, prepared from the amine and acetyl chloride in dry pyridine, had m. p. 94—95° after crystallisation from ligroin (b. p. 40—60°), and did not depress the melting point of a genuine specimen.

The benzoyl derivative reacts readily, after a short induction period, with bromine (1 mol.) in chloroform to yield hydrogen bromide and a complicated product, containing free benzoic acid, which is being further investigated.

5-*Benzoyloxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentan*-1-*one* (VIII) cryst-

allises from ligroin (b. p. 40—60°) or methyl alcohol in lustrous plates having m. p. 60°, which is unchanged by further crystallisation (Found: C, 73·5; H, 8·1. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%).

Hydrolysis with aqueous-alcoholic sodium hydroxide for 1 hour at 100° yielded the hydroxy-ketone, m. p. 142°, mixed m. p. 142°. This identity was confirmed by conversion into the *p*-nitrophenylhydrazone.

An oily *oxime* was obtained when 1 g. of the derivative, 1 g. of hydroxylamine hydrochloride, and 1·2 g. of anhydrous sodium acetate were heated together in absolute-alcoholic solution on the steam-bath for 3 hours. As the oil could not be induced to crystallise, it was converted into the *benzoyl-oximino*-derivative with benzoyl chloride in dry pyridine solution. This substance was obtained as an oil, b. p. 200—215°/15 mm. (Found: C, 73·8; H, 6·4. $C_{23}H_{25}O_4N$ requires C, 72·8; H, 6·6%).

Reduction of the benzoyloximino-derivative, b. p. 200—215°/15 mm. This was carried out with 2·5% sodium amalgam and glacial acetic acid, as in the previous case. The product was oily, probably containing much 5-hydroxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine; it was therefore reduced with hydriodic acid and phosphorus for 2 hours, and the liquid made alkaline and steam-distilled. The amine obtained on extraction of the distillate with ether was identified as 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine by means of its picrate, m. p. 236—238° (decomp.); mixed m. p. with a genuine specimen 238° (decomp.).

The benzoyl derivative, m. p. 60° (in contrast with its isomeride, m. p. 105°) is unaffected by bromine in chloroform or in glacial acetic acid at all temperatures up to the boiling points of these solvents.

Oximation of the Hydroxy-ketone.—The hydroxy-ketone (1·5 g.), hydroxylamine hydrochloride (0·7 g.), and anhydrous sodium acetate (0·85 g.) were heated together in absolute-alcoholic solution on the steam-bath for 2 hours. The product was cooled, diluted with much water, and extracted with ether; the ethereal extract was washed with sodium hydrogen carbonate solution, dried, and evaporated. The mixture of oily oximes obtained (Found: C, 64·1; H, 9·9. $C_9H_{17}O_2N$ requires C, 63·2; H, 10·0%) could not be induced to crystallise after some weeks. Treatment with hydrogen chloride in ether at 0° yielded a small amount of a crystalline hydrochloride, m. p. 61—63° (not analysed). The oily mixture (0·3 g.), when benzoylated with excess of benzoyl chloride in dry pyridine, yielded a yellow oil, which partly crystallised after being kept in a vacuum for a week. After being drained from the residual oil and washed with and crystallised from ligroin (b. p. 80—100°), the substance was obtained in clusters of short prisms, m. p. 135°. It was identi-

fied as the benzoyl-oximino-derivative of 1-benzoyloxy-2 : 2 : 3 : 3-tetramethyl*cyclo*pentan-5-one by direct comparison and the method of mixed melting points. An oil accompanied it which probably consisted of the isomeric benzoyl-oximino-derivative, b. p. 200—215°/14 mm. (see below).

On reduction of the mixture of oily oximes with $2\frac{1}{2}\%$ sodium amalgam in glacial acetic acid, and treatment of the product with ethereal picric acid, a mixture of 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine and 3 : 3 : 4 : 4-tetramethyl*cyclo*pentylamine picrates was obtained, which melted at 243—245° (unchanged on recrystallisation) and depressed the melting points of both pure isomerides. Treatment with acetic anhydride and anhydrous sodium acetate yielded a mixture of *acetyltetramethyl*cyclo*pentylamines*, m. p. 79—85°. A similar mixture was obtained on oximation, reduction, and acetylation of the mixture of tetramethyl*cyclo*pentanones obtained from the hydroxy-ketone (p. 1663) (Found: C, 70·5, 70·4; H, 11·5, 11·5; N, 7·4, 7·4). $C_{11}H_{21}ON$ requires C, 72·1; H, 11·4; N, 7·6%). The mixture is much more soluble than either of the pure isomerides: a synthetic mixture of these has m. p. 83—85°.

1 (*or* 5)-*Methoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentan*-5 (*or* 1)-*one*.—The hydroxy-ketone can be methylated with methyl sulphate and 10% sodium hydroxide solution by treatment on the steam-bath for $1\frac{1}{2}$ hours. On fractionation, a colourless oil, b. p. 94°/14 mm., was obtained, almost the whole of the product passing over at this temperature. A small residue, which solidified, consisted of unchanged hydroxy-ketone. On redistillation, a fraction, b. p. 88—90°/10 mm., $n_D^{19°}$ 1·4574, was obtained (Found: OMe, 18·0. $C_{10}H_{18}O_2$ requires OMe, 18·2%).

On reduction with hydriodic acid 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone, isolated as the semicarbazone, m. p. 224° (decomp.), was formed. Characteristic solid derivatives could not be prepared; but treatment with hydroxylamine acetate in absolute-alcoholic solution yielded an oily *oxime*, which on reduction in the usual manner was converted into 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine. Thus the main constituent appears to be the 5-methoxy-ketone; it cannot be asserted, however, that the isomeric 1-methoxy-ketone is not present.

The author wishes to express his thanks to Professor C. K. Ingold, F.R.S., for his continued interest and helpful criticism, and to the Royal Commissioners of the 1851 Exhibition for a Senior Studentship.

THE UNIVERSITY, LEEDS. [*Received, March 22nd*, 1928.]

CCXIX.—*Anomalous Rotatory Dispersion from the Standpoint of the Drude Equation.*

By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS.

ALTHOUGH the rotatory dispersion of ethyl and methyl tartrates has been investigated exhaustively (Lowry and Dickson, J., 1915, **107**, 1173; Lowry and Abram, *ibid.*, p. 1187; Patterson, J., 1916, **109**, 1139, *et seq.*; Winther, *Z. physikal Chem.*, 1902, **41**, 177, etc.) both in the homogeneous condition and in solution, yet relatively little research has been done on the dispersion of the simple derivatives of these two esters. A series of derivatives was therefore prepared in order to see whether the anomalous dispersion shown by the parent esters persisted in the derived compounds, or whether the dispersion passed from anomaly to complexity or to simplicity in a definite manner in the two series; also, to gain further information on the relationship of dispersion to relative configuration and their interpretation in terms of the Drude equation.

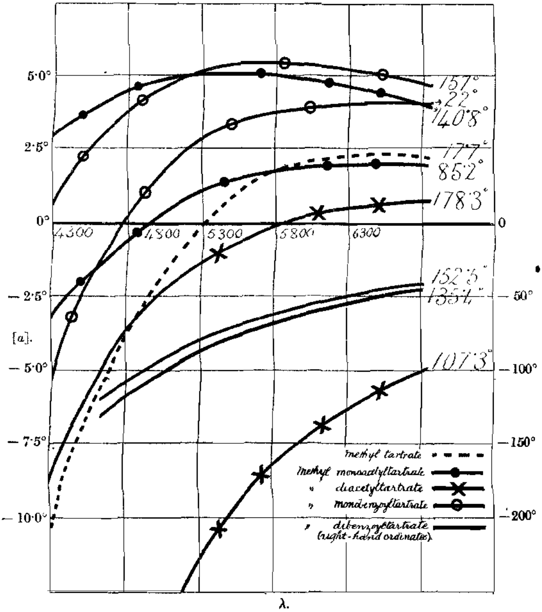
Anomalous Rotatory Dispersion and Relative Configuration.

Examination of the rotatory dispersion curves for the compounds shows that (*a*) both inflexion and maxima are confined to the positive region of rotation, and (*b*) crossing of the axis occurs in one way only, *viz.*, as the wave-length decreases so the rotation decreases, $d\alpha/d\lambda$ being always positive.

Fig. 1 shows that methyl *d*-tartrate and its monoacetyl, diacetyl (at 178·3° only), and monobenzoyl derivatives exhibit visual anomaly in the positive region of rotation, and further, when crossing of the axis occurs, $d\alpha/d\lambda$ is positive. The disposition of the dispersion curves for the dibenzoyl derivative is given on the diagram; they do not show visual anomaly.

Fig. 2 indicates that inflexion of the dispersion curves in the positive region of rotation was realised for the mono- and di-acetyl and monobenzoyl derivatives of ethyl tartrate; inflexion of the dispersion curves for the ester itself occurs at higher temperatures than shown in the diagram. Maxima occur in the positive region for ethyl tartrate and its mono- and di-acetyl and monobenzoyl derivatives. The diacetyl derivative, like the parent ester, shows crossing of the axis. The dispersion curves for the dibenzoyl derivative, for the range of temperature and wave-length examined, are situated in the negative region. On the same diagram is indicated the disposition of the dispersion curves for the thionyltartaric and dichlorosuccinic esters.

Fig. 1.



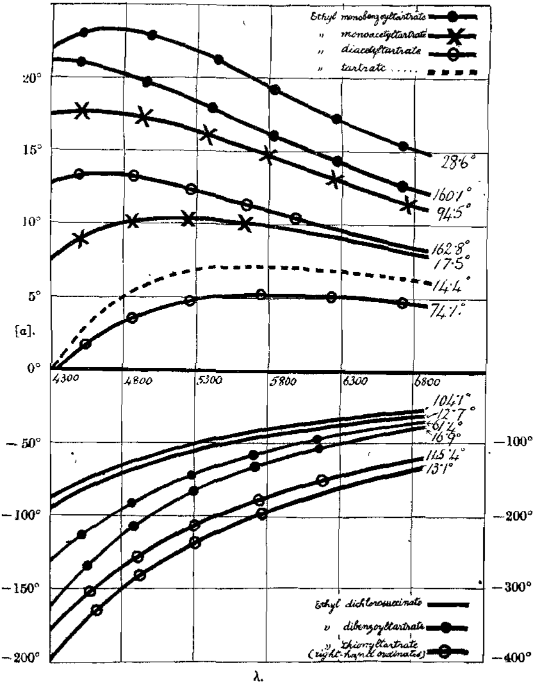
Methyl tartrate and certain derivatives.

The types of dispersion of the compounds examined are given below:

	Dispersion.		Dispersion.
Methyl tartrate	Anomalous	Ethyl tartrate	Anomalous
Monoacetyl derivative	Anomalous	Monoacetyl derivative	Anomalous
Diacetyl derivative ... (at the higher temperature)	Anomalous	Diacetyl derivative ...	Anomalous
Monobenzoyl derivative	Anomalous	Monobenzoyl derivative	Anomalous
Dibenzoyl derivative ... (negative region)	Complex	Dibenzoyl derivative ... (negative region)	Complex
		Thionyl derivative ...	Simple in region of spectrum examined.
		Ethyl dichlorosuccinate	Simple in region of spectrum examined.

In general, the dispersions of the simple acetyl and benzoyl derivatives of the two series are closely related, but comparison of

Fig. 2.



Ethyl tartrate and certain derivatives.

the two diagrams shows that the crossing of the axis and, consequently, maxima are removed to a shorter wave-length in passing from methyl tartrate and its derivatives to ethyl tartrate and its

derivatives, a fact which is well illustrated by the diacetyl derivatives of the two series.

Lowry (J., 1915, **107**, 1195), having proved conclusively the validity of the Drude equation, quotes inflexion, maxima, and crossing of the axis as visual criteria for anomalous dispersion, but this investigation and a survey of the literature indicate that the above three points are also criteria for relative configuration. Thus for *d*-tartaric acid and its derivatives the mode of crossing the axis is always the same, points of inflexion occur only in the positive region of rotation, and, in all cases, maxima are confined to the positive region.

The dispersion curves for methyl diacetyltartrate are of particular interest; they form a series of curves which approach the axis from the negative side with increasing temperature, and the curve obtained at 178·3° crosses the axis towards the red end of the spectrum. A solution of ethyl tartrate in carbon tetrachloride (Lowry and Dickson, *loc. cit.*) affords a similar case. The curves do not become asymptotic to the zero axis in the negative region.* It is hard to reconcile this phenomenon, which is not confined to these cases, with the founding of a general explanation of optical rotation on a Drude equation with the infra-red term omitted. Although quantitative measurements have justified such procedure, yet the theoretical significance is lost. The infra-red term is associated with the configuration, and should be regarded as the relative configuration term. For a compound of "*d*" configuration it is negative, and for a compound of "*l*" configuration positive. It is this term which prevents dispersion curves in the negative region, for a compound of relative configuration denoted by "*d*," becoming asymptotic to the zero axis in that region towards the red in the visible and non-visible region of the spectrum; and thus, by the influence of the infra-red term, the curve is drawn over the axis into the positive region.

In the case of a compound of "*d*" configuration in the *positive* region, no instance can be traced where intersection of the zero axis, $d\alpha/d\lambda$ being negative, occurs; the approach, as the curve passes into the red end of the spectrum, appears to be asymptotic in character either to the zero axis, or to an axis parallel to the zero axis in the positive region.

In cases where the dispersion curve does not actually pass over

* The dispersion curve for the same compound in ethylene dibromide does not cross the axis in the visible region, and extrapolation by means of the two-term equation shows that crossing of the zero axis does not occur, but that the dispersion curve becomes asymptotic to the zero axis in the negative region.

into the negative region, its approach to the zero axis is a sufficient guide for relative configuration, provided that the *approach* is towards the *blue* end of the spectrum. Many instances are given in the two diagrams of experimental results (Figs. 1 and 2).

Methyl and ethyl dibenzoyltartrates, ethyl dichlorosuccinate and ethyl thionyltartrate have rotations removed from the axis on the negative side. The first two compounds have been obtained by simple chemical reactions not prone to give rise to a Walden inversion, hence their relative configuration is taken as " *d*." The configuration of dextrorotatory * dichlorosuccinic acid and its ethyl ester (for comparison of preparation and optical rotation, see Darzens, *Compt. rend.*, 1912, **154**, 1615; Holmberg, *Svensk Kem. Tidsk.*, 1912) has been discussed by Clough (J., 1918, **113**, 526), who, on the basis of the relationship between optically active α-amino- and α-hydroxy-acids, regards this acid as of relative configuration " *l*." The relative configuration of the thionyl ester, which is an intermediate product in the preparation of the dichloro-ester, is assumed to be " *d*."

Experiments with solvents failed to reduce the high rotation of the last two esters sufficiently for observations to be taken in the anomalous region. This is to be expected, for optically active compounds only exhibit great sensitiveness to both temperature and solvents near or in the region of anomalous rotatory dispersion.

Interpretation of Anomaly by the Drude Equation.

In the consideration of the Drude equation, R. W. Wood ("Physical Optics," p. 492), from theoretical considerations, indicates that the anomalous rotatory dispersion of tartaric acid is due to an infra-red lævorotatory electron and an ultra-violet lævorotatory electron. This view has been rejected by Lowry (Lowry and Cutter, J., 1925, **127**, 604), who, from quantitative measurement, expresses the rotatory dispersion " as the sum of two simple partial rotations of which the characteristic frequencies are both in the ultra-violet region," the two partial rotations being of opposite sign. Lowry, however, admits the theoretical possibility of " spurious anomaly " in transparent media.

The view here put forward is that both explanations of the phenomenon are incomplete, and it is considered that anomaly is due to one or more rotations of electronic origin in the ultra-violet, and a rotation of molecular origin, due to atomic oscillations, in the infra-red.

* The compound investigated was lævorotatory, *i.e.*, of opposite relative configuration.

The total rotation of the plane of polarisation being expressed in the usual way as a summation of terms,

$$\alpha = \sum \frac{k}{\lambda^2 - \lambda_0^2}$$

each term, except the infra-red term, represents the contributary rotation due to ultra-violet electrons, active in rotating light. The infra-red term, however, represents rotation referred to molecular origin. Observations on selective reflexion and absorption have shown that characteristic frequencies in the ultra-violet arise from electrons, whereas those in the infra-red, which in many cases pass into the region of short electric-discharge waves, are referred to atomic oscillations.* The contributary rotation due to this infra-red term, although small in the visible region, is definite, and, being of molecular origin, gives rise to dextrorotatory or lævorotatory dispersion according as the relative configuration is "*d*" or "*l*." The importance of this configuration term as a fundamental part of the Drude equation is considered below.

Case I. The infra-red term contributes a dextrorotatory dispersion which is of lævorotatory molecular origin, and which manifests itself in the near infra-red through the oscillations of the constituent atoms (or atomic groups),† and the ultra-violet term contributes a dextrorotatory dispersion of a dextrorotatory electron (or system of electrons):

$$\alpha = \underset{\text{(ultra-violet)}}{\frac{k_1}{\lambda^2 - \lambda_1^2}} - \underset{\text{(infra-red)}}{\frac{k_2}{\lambda^2 - \lambda_2^2}}$$

The condition is shown diagrammatically in Fig. 3, the upper set of curves showing the two simple rotations, and the lower the resultant curve. The dotted lines ‡ represent the unrealisable regions of the spectrum in the red, infra-red, and ultra-violet.

The realisable curve shows no anomaly in the visible spectrum, for minima in the positive region of rotation have not been realised.

* Compare Haas, "Introduction to Theoretical Physics," Vol. ii, 1925, section on "General theory of spectra and of atomic structure"; Lecomte, "Contribution à l'étude de l'absorption des rayons infra-rouges par les composés organiques," La Lino-Générale, Paris; Baly, "Spectroscopy," Vol. I, p. 217 (1927); Coblentz, "Investigations of infra-red spectra," Carnegie Institution of Washington, 1905, **35**, 117.

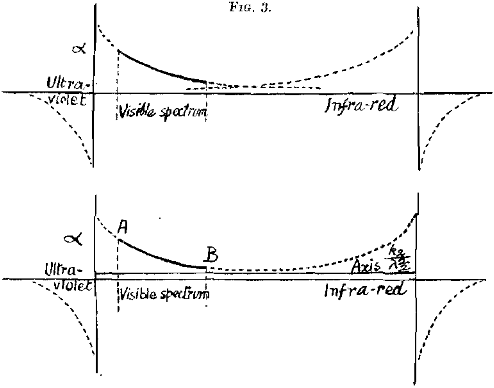
† Compare Bjerrum's theory; also Lorentz, "Lectures on Theoretical Physics," Vol. ii, p. 395 (1927).

‡ The dotted portion of the lower curves for longer wave-lengths in Figs. 3 and 4, if realisable, would represent those parts where the infra-red term is no longer functioning as a constant, the ultra-violet term at the same time passing to a constant value. The complete curve represents, according to the part considered, either simplicity, complexity, or anomaly.

The rotatory dispersion is always positive; the curve tends to become asymptotic and not to cut the axis. Even Ingersoll (*Physical Rev.*, 1917, **9**, No. 4, 257), who investigated the infra-red, did not realise the asymptotic portion of the dispersion curve.

The rotation due to the dextrorotatory electron dies down with increasing wave-length, whilst that due to molecular rotation

FIG. 3.



increases in effect. No apparent deviation from simplicity occurs in the visible spectrum, for

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda_2^2},$$

where k_2/λ_2^2 is a *constant representing an* axis k_2/λ_2^2 *above the zero* axis to which the dispersion curve would ultimately tend to become asymptotic.

Case 2. The infra-red term contributes a dextrorotatory dispersion as before, but the ultra-violet term contributes a lævorotatory dispersion due to a lævorotatory electron (or system of electrons):

$$\alpha = -\underset{\text{(ultra-violet)}}{\frac{k_1}{\lambda^2 - \lambda_1^2}} - \underset{\text{(infra-red)}}{\frac{k_2}{\lambda^2 - \lambda_2^2}}$$

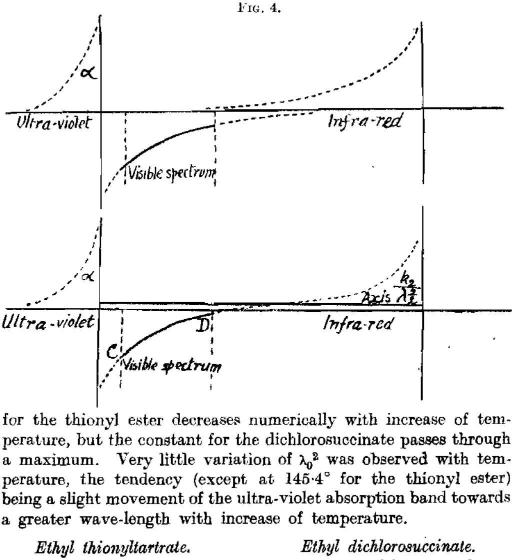
This condition is shown in Fig. 4. The effect due to the infra-red term is slight, and departure from simplicity cannot be detected. The constant k_2/λ_2^2 represents an axis parallel to the zero axis in the *positive* region; it is the axis to which the curve tends to become

asymptotic and which it finally cuts in the unrealisable region on proceeding up to the band.

The constant in both cases is positive and is the "d" configuration constant. The above two cases represent simplicity in the positive and negative regions, respectively.

The two compounds mentioned below are examples of Case 2. They were found to be simple over a wide range of temperature. Under the experimental conditions the small constant infra-red contribution could not be differentiated. The rotational constant

FIG. 4.



for the thionyl ester decreases numerically with increase of temperature, but the constant for the dichlorosuccinate passes through a maximum. Very little variation of λ_0^2 was observed with temperature, the tendency (except at 145·4° for the thionyl ester) being a slight movement of the ultra-violet absorption band towards a greater wave-length with increase of temperature.

Ethyl thionyltartrate.

Temp.	λ_0^2.	k.
13·1°	0·04264	56·18
20·3	0·04350	55·46
42·3	0·04356	54·09
56·9	0·04326	53·33
82·6	0·04448	51·96
116·9	0·04452	51·08
125·2	0·04440	50·56
145·4	0·04318	50·28

Ethyl dichlorosuccinate.

Temp.	λ_0^2.	k.
12·7°	0·04992	12·61
22·6	0·04950	12·66
41·4	0·04979	12·67
62·4	0·04991	12·51
87·0	0·05141	12·13
104·1	0·05165	11·88

The introduction of another ultra-violet term of the same sign into equations under Cases 1 and 2 gives the condition for complexity. The dispersion curve in the visible region now represents the summation of three simple curves, although the contribution by the infra-red term may not be detectable quantitatively. The *dispersion curves in the negative and positive regions, respectively*, take corresponding paths in the infra-red, *via* an axis k/λ_2^2 similar to *those taken by the curves expressing simplicity. This directive* molecular influence, though of little magnitude in the visible region, *dominates the final direction of the dispersion curve.*

Figs. 3 and 4 illustrate complexity when AB and CD represent the summation of two simple electronic curves of like sign, together with the small molecular contribution.

The introduction of an ultra-violet term of opposite sign into Cases 1 and 2 gives rise to anomaly; the positive term must, however, be associated with the high-frequency constant. The compounded curve produces under certain conditions the three cases of visible anomaly. In all cases the curves eventually take a path, *via* the axis k_2/λ_2^2, up to the band.

Curves wholly in the positive region never touch the zero axis. Curves in the negative region cross the zero axis.

Anomaly is illustrated by Fig. 5, EF being the compounded curve obtained by the introduction of a term of opposite sign. This curve shows that crossing of the zero axis occurs in one way only, $d\alpha/d\lambda$ being positive, and that anomaly (maxima and inflexion) is confined to the positive region. Curves crossing the axis ($d\alpha/d\lambda$ negative) or showing maxima or inflexion in the negative region could only arise from a compound of "*l*" configuration, for the electronic and molecular dispersion curves form one continuous function, and reversal of the electronic part implies reversal of the molecular portion of the dispersion curve. Such curves belong to a general type of curve represented by the mirror image of the curve in Fig. 5.

Although quantitative measurements show that the infra-red term is practically negligible in the visible region, yet its importance must not be under-rated, for it determines the path to the infra-red band. *This restriction to a particular path* places upon the occurrence of anomaly those limitations which are such valuable criteria *for the determination of relative configuration.*

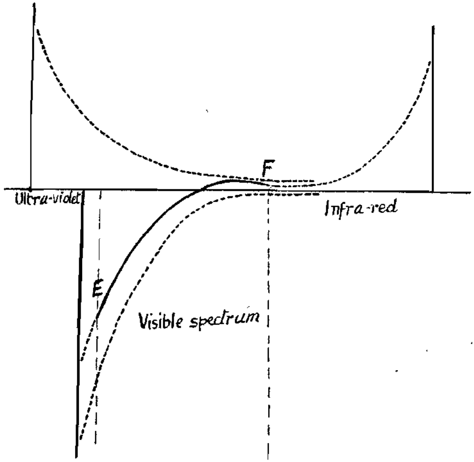
Methyl diacetyltartrate is an interesting example of visual anomaly occurring towards the red end of the spectrum. From 107·3° to 171·5°, inclusive, the dispersion curves lie wholly in the negative region, whilst at 178·3° crossing of the axis from the negative to the positive region takes place between λ 5893 and

λ 5590. Increase of temperature has caused the crossing to move from infra-red into the visible region; the approach to the zero axis of the curves in the negative region is *not* asymptotic in character.

The further movement of crossing from the visible spectrum into the ultra-violet is shown by methyl monobenzoyltartrate:

Temp.	22·0°	57·0°	80·8°
Crossing of zero axis at λ...	4861—4678	4678—4455	4455—4359

Fig. 5.



For higher temperatures the curves lie wholly in the positive region, the crossing having moved into the ultra-violet. Simultaneously with the movement of the crossing there occur the development and then the movement of maxima (see Experimental). Crossing and maxima form part of a continuous curve, the maxima always occurring at a greater wave-length than the crossing.

Lowry (J., 1915, **107**, 1195) has discussed the limiting condition for anomalous dispersion on the assumption that an infra-red band is absent. From the foregoing considerations it follows that the limiting condition requires modification, *viz.*, the high-frequency term may have the rotation constant k not only greater than but

also equal to k_1, the rotational constant of the low-frequency ultra-violet term. When $k = k_1$ the curve may cut the zero axis in the visible region, for the contribution due to the molecular rotation, though small, is of appreciable magnitude. The importance of the infra-red term is that it prevents such dispersion curves becoming asymptotic to the zero axis.

In all cases of anomaly the smaller ultra-violet dispersion constant (high frequency), regardless of the value of k, is associated with the positive ultra-violet term for a compound of "*d*" configuration, and with the negative ultra-violet term for a compound of "*l*" configuration. Reference to the sign of the infra-red term is only necessary for determining configuration in the cases of simplicity and complexity.

The Infra-red Term and the Relative Configuration of Quartz.

Quartz affords an interesting example, since the infra-red term has been included in the equation expressing its dispersion (Lowry, *Phil. Trans.*, 1913, *A*, **212**, 261). The term is positive for left-handed quartz; this variety is accordingly configuratively related to *l*-tartaric acid.

The configuration can be deduced, however, without considering the infra-red term; the high-frequency constant (omitted on account of its small magnitude) is associated with the negative ultra-violet term. Similar reasoning, from data given by Lowry and Cutter (J., 1925, **127**, 604) for *d*-camphor, shows that it is configuratively related to left-handed quartz.

The wave-length of the "Reststrahlen" from qnartz, as determined by Porter (*Astrophys. J.*, 1905, **22**, 227), is 8·28 μ; Rubens and Nichols (*Ann. Physik*, 1897, **60**, 418) found that reflexion took place at three points of the spectrum, 8·5 μ, 9·02 μ, and 20·75 μ; Lowry, in the application of the Drude equation to the rotatory power of quartz, gives $(8{\cdot}84)^2$ μ as the dispersion constant in the infra-red term and states that "the infra-red absorption is an essential factor in determining the optical rotation in quartz both in the infra-red and in the visible region of the spectrum." Waves whose frequencies differ little from a characteristic frequency are strongly reflected and absorbed; further, infra-red frequencies are referred to atomic oscillations.

Physical Interpretation of the Infra-red Term and Anomaly.

Thomson (*Phil. Mag.*, 1920, **40**, 720) has deduced a general expression for the rotation of the plane of polarisation, due to the scattering of light by electrons, on the assumptions that (1) the whole molecule rotates as a rigid body, and (2) there is no displace-

ment of the electrons relative to the atoms in the molecule. He shows that molecules representing enantiomorphs rotate in opposite directions, and calculates the contribution, due to the rotation of the molecule, to the optical rotation. This calculated rotation is less than 12′ specific rotation per cm., thus the molecular contribution is only a small part of the optical rotation generally observed. The contribution to the rotation of quartz by the infrared term for λ 5896 is 10·3′ per mm. (compare Lowry, *loc. cit.*).

Since the whole molecule, rotating as a rigid body, does not give sufficient movement to account for the rotation produced by optically active compounds, Thomson regards the molecule as made up of two parts: (1) the atomic tetrahedron formed by the atoms or groups round the asymmetric carbon atom, and (2) the electronic tetrahedron formed by the structural electrons round the asymmetric carbon atom. The displacement of the atomic tetrahedron in response to light waves in the visible spectrum will be small in comparison with that of the much lighter tetrahedral arrangement of the electrons.

A system of electrons, α, β, γ, and δ, is considered, each electron being situated at the corner of a tetrahedron. If the restoring forces for α and β are large compared with those for γ and δ, the two electrons γ and δ would rotate round the axis αβ when acted on by light. The rotation due to this single electronic tetrahedron is found to give values comparable with the rotation given by optically active compounds. The volume of the tetrahedron, which measures the optical rotation of a single molecule, vanishes in the following cases: (1) γδ is parallel to αβ; (2) γδ intersects αβ; (3) γδ is at right angles to αβ (regular tetrahedron). A shift in the position of one or both of the electrons γδ might change the sign of the optical rotation produced by the molecule. A compound, by temperature or solvent action, may change its sign of rotation owing to electronic displacements, but not the sign of the contributary molecular rotation unless change of configuration takes place.

The expression which Thomson obtains for the rotations of each tetrahedron, electronic and atomic, we regard as representing the ultra-violet and infra-red terms, respectively, of the Drude equation. An extension of this view, considering eight electrons instead of four round the asymmetric carbon atom, would give rise to two electronic tetrahedra and would afford a physical insight into the meaning of complexity and anomaly, as expressed by the Drude equation. The displacement of the electronic tetrahedra in opposite directions would give rise to anomaly; in the same direction, to complexity; in the same direction and acting as a single tetra-

hedron, to simplicity. On this view, one asymmetric centre in a *molecule is sufficient to account for the various classes of dispersion.*

Tschugaeff (*Trans. Faraday Soc.*, 1914, **10**, 35) states that "it is *by no means necessary that the* electrons *in* the *four* radicals and in the central atom should rotate in the same direction. Consequently it seems to be possible that certain bodies containing but one asymmetric carbon atom can exhibit anomalous rotatory dispersion."

Drude ("Optics," p. 415) states that "in general every active substance must show anomalous * rotatory dispersion in certain regions of vibration, but these regions do not necessarily lie within the limits of the vibrations which can be produced experimentally," and this statement occurs immediately after reference to cases of anomalous rotatory dispersion mentioned by Landolt ("Das optische Drehungsvermögen").

It is important to summarise the classes of anomaly:

(1) True anomalous rotatory dispersion occurring at the crossing of an absorption band which is of optically active electronic origin.

(2) Anomalous rotatory dispersion due to the superposition of two simple rotations of opposite sign, the characteristic frequencies being both in the ultra-violet.

(3) Spurious anomalous rotatory dispersion, *i.e.*, dispersion occurring between two bands.

(4) Type discussed in paper on co-ordination compounds (this vol., p. 1727).

Discussion of Different Types of Anomalous Rotatory Dispersion.

The view that a single asymmetric centre can give rise to anomaly makes class (*f*) (ii) (Lowry and Cutter, *loc. cit.*) ("existence of two natural frequencies in a single molecule") a fundamental class. The recognition of this class is regarded by the above authors as a *matter of pure speculation, in spite of the increasing number of* cases in which a single asymmetric centre shows anomaly, this conclusion being based on the fact that there is no experimental proof of a single asymmetric centre, having two frequencies, giving rise to two absorption bands.

Such a demand is unjustifiable, since no case is known (even when more than one asymmetric centre is in a single molecule), where two bands, corresponding to a high and a low frequency and satisfying the demands of the Drude equation, have been located experimentally. In those cases in which the low-frequency band has actually been determined, the high-frequency band, in the case of anomalous or complex compounds, has been inferred. Accord-

* "Anomalous" should be interpreted to include also "spurious anomalous," which is defined by Frankland (*Trans. Faraday Soc.*, **1914**, **10**, 91).

ingly, the experimental determination of the low-frequency and the inference of the presence of the high-frequency band for a single molecule with one asymmetric centre, is sufficient (and the only available) proof to satisfy the demand.

(*a*) *d*-γ-Nonyl nitrite (Pickard and Hunter, J., 1923, **123**, 434) with absorption band λ 3670—3720, though not anomalous, has a single asymmetric centre which possesses two natural frequencies, giving rise to two bands.

(*b*) For potassium chromium oxalate, $[Cr(C_2O_4)_3]K_3$ (Jaeger and Thomas, *Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 693), the molecular rotation passes through a maximum about λ 5200 and through a minimum about λ 5700 in passing through the band. The compound thereafter shows visual anomaly to the right of the band, *viz.*, on the long wave-length side of the band.

Asymmetric centres of the same relative configuration occurring in a single molecule give rise to the same phenomenon as class (*f*) (ii) the dispersion exhibited being a summation effect; instances are methyl and ethyl *d*-tartrates and *l*-β-octyl oxalate (Lowry and Richards, J., 1924, **125**, 1593). The bands are far removed in the ultra-violet and have not been determined experimentally, but the dispersion has been measured and the results expressed by equations involving two terms of opposite sign (Lowry and collaborators, *locc. cit.*). In these cases the two centres of activity are of identical type. Methyl and ethyl diacetyl-*d*-tartrates are further examples since they show visual anomaly. Methyl and ethyl monoacetyl- and monobenzoyl-tartrates are examples of compounds having two centres of " *d* " configuration with different rotatory power, showing visual anomaly.

When the two asymmetric centres are of different configuration, the resulting anomaly expresses the configuration of the dominant centre. When more than two centres are present, the dispersion curve represents a summation effect.

d-*sec.*-Butyl *d*-lactate (Wood, Such, and Scarf, J., 1926, 1928) exhibits anomaly in the negative region, the dominant centre being the lactate radical. A case of historical interest, though the radicals involved are both of the same relative configuration (" *l* "), is menthyl camphor-β-sulphonate, the dispersion of which was investigated by Tschugaeff (*Ber.*, 1911, **44**, 2023). Menthyl triphenylacetate (*idem, ibid.*, 1912, **45**, 2759) is anomalous in the negative region of rotation; camphor-β-sulphonic acid is potentially anomalous (Lowry, J., 1925, **127**, 1503), the high-frequency term being negative. The ester menthyl camphor-β-sulphonate is anomalous, and, as would be expected, in the negative region (" *l* " configuration).

For over ten years, it has been the convention to assign compounds containing one asymmetric centre and compounds containing *asymmetric centres of identical type, showing anomaly*, to class (*c*): "Formation of two molecular types from one optically active compound." The origin of this class can be traced to the view, put forward by Arndtsen in 1858, explaining the anomalous rotatory dispersion of solutions of *d*-tartaric acid. The present tendency, however, is to seek a cause for a partial rotation of opposite sign in the molecule itself. Such centres of opposite sign have been assumed, on the theory that an unsaturated group in an asymmetric molecule may acquire an induced asymmetry [type (*e*), "induced asymmetry in unsaturated molecules," Lowry, *loc. cit.*].

The necessity for seeking, either by isomeric change or by induced asymmetry, a centre giving rise to an opposite partial rotation is due to the non-recognition that a single asymmetric centre can give rise to two electronic components (two electronic tetrahedra) which may contribute rotations of the same or opposite sign.

The carbonyl group in camphor is considered optically active by induced asymmetry, and the rotation contributed by this hypothetical centre is 71·05° (*d*-camphor in acetone, λ 5893). This is the contribution due to the low-frequency term, whereas the high-frequency term only contributes 20·54°. A theory which attaches importance to a hypothetical centre needs scrutiny. More serious than the assumption of a rotational value is the point that the *carbonyl group has been considered asymmetric in order that it* might be a decisive factor with respect to determining the relative configuration of the molecule.

The carbonyl group need not be regarded as an asymmetric centre but rather as causing a deflecting and disturbing action on the electronic system round the asymmetric centre. The nearer the carbonyl group is to the asymmetric centre the greater will be the effect on the electronic tetrahedra (compare Tschugaeff's views on rotatory dispersion, *Trans. Faraday Soc.*, *loc. cit.*, p. 35, with regard to the influence of the electrons attached to the radicals and the asymmetric carbon atom).

Quartz has been placed provisionally in class (*f*) (i) ("Crystals with two natural frequencies"), since class (*f*) (ii) has been discarded. On the view here expressed, quartz falls naturally into this class. Thomson (*loc. cit.*) has applied the same general equation to quartz as to organic compounds. Molecules, in the crystalline condition, can be optically active, owing to distortion, although inactive when fused or in solution. This distortion will be reflected in the arrangement of a system of electrons round the silicon atoms, and anomaly may result.

In β-quartz, Bragg and Gibbs (*Proc. Roy. Soc.*, 1925, **109**, 405) find that the oxygen atoms are placed almost exactly in a tetrahedral arrangement round the silicon atom, and they consider that silicon, being a quadrivalent atom, is probably striving for such an arrangement. In addition, Gibbs (*ibid.*, 1926, **110**, 443) has pointed out that, in passing from β- to α-quartz, the tetrahedrally arranged oxygens have been twisted and slightly distorted with consequent loss of symmetry, which is in accordance with the rotation data (for sodium light):

$$\underset{21\cdot7^\circ\ (20^\circ\text{C.})}{\alpha\text{-Quartz}} \xleftrightarrow{575^\circ} \underset{2\cdot52^\circ\ (600^\circ\text{C.})}{\beta\text{-Quartz}}$$

The explanation offered of the pyro- and piezo-electric effects of quartz by the suggested structure rests on the assumption of electric doublets, one corresponding to each valency. This is in harmony with the assumption that the eight structural electrons round the silicon atom form two tetrahedral arrangements.

EXPERIMENTAL.

Ethyl Tartrate.—The ester was prepared by the continuous esterification process (Aston and Frankland, J., 1901, **79**, 511) and fractionated ten times in a vacuum. After the seventh distillation the ester exhibited a transient yellow colour and the distillates in the subsequent fractionations behaved similarly. B. p. 155—156°/15 mm. Rotations were taken in a 3-dcm. tube.

Densities determined:

t°	0·2	28·06	61·51	106·9	149·45
$d_{4^\circ}^{t^\circ}$	1·2246	1·1961	1·1621	1·1155	1·0720

$d_{4^\circ}^{0·8^\circ}$ 1·2239.		$d_{4^\circ}^{14·4^\circ}$ 1·2101.		$d_{4^\circ}^{20^\circ}$ 1·2044.		$d_{4^\circ}^{40^\circ}$ 1·1840.	
λ.	$[\alpha]_\lambda^{0·8^\circ}$.	λ.	$[\alpha]_\lambda^{14·4^\circ}$.	λ.	$[\alpha]_\lambda^{20^\circ}$.	λ.	$[\alpha]_\lambda^{40^\circ}$.
6438	+5·28°	6152	7·01°	5893	7·83°	5590	10·22°
6364	5·31	5893	7·16	5700	7·90	5461	10·35
6152	5·31	5770	7·18	5613	7·90	5344	10·40
5893	5·31	5700	7·19	5590	7·91	5334	10·41
5770	5·31	5639	7·19	5538	7·90	5323	10·41
5700	5·28	5590	7·18	5324	7·78	5292	10·40
5590	5·12	5461	7·10			5086	10·27

$d_{4^\circ}^{60^\circ}$ 1·1635.		$d_{4^\circ}^{80^\circ}$ 1·1430.		$d_{4^\circ}^{100^\circ}$ 1·1226.		$d_{4^\circ}^{120^\circ}$ 1·1022.		$d_{4^\circ}^{140^\circ}$ 1·0817.	
λ.	$[\alpha]_\lambda^{60^\circ}$.	λ.	$[\alpha]_\lambda^{80^\circ}$.	λ.	$[\alpha]_\lambda^{100^\circ}$.	λ.	$[\alpha]_\lambda^{120^\circ}$.	λ.	$[\alpha]_\lambda^{140^\circ}$.
5324	12·40°	5086	14·57°	4861	16·23°	4722	17·76°	4678	18·78°
5154	12·52	4964	14·68	4786	16·30	4678	17·80	4587	18·86
5105	12·55	4926	14·70	4722	16·31	4587	17·81	4510	18·87
5086	12·55	4861	14·72	4678	16·31	4510	17·76	4472	18·85
4926	12·54	4786	14·69	4587	16·24				
4861	12·46	4678	14·61						

Ethyl Monoacetyltartrate.—This derivative was prepared by a modification of the method given by Patterson (J., 1900, **77**, 1099). Acetyl chloride (14 g.; slightly less than the calculated amount), in three times its volume of benzene, was added 1 c.c. at a time to 40 g. of ethyl tartrate dissolved in 30 c.c. of benzene. After each addition the mixture was shaken vigorously and heated to 80° until hydrogen chloride ceased to be evolved, then cooled to ordinary temperature, and the process repeated. After all the acetyl chloride had been added the benzene was removed, the residue distilled under diminished pressure, and the distillate collected at 165—170°/15 mm. The distillate was shaken with 5 c.c. of water and separated. This was repeated eight times in order to remove ethyl tartrate. The residual oil was dissolved in a large volume of water and cooled to 0°: the ethyl diacetyltartrate which separated was filtered off and the filtrate extracted with chloroform. The extract was dehydrated over anhydrous sodium sulphate and the solvent removed at the ordinary temperature. The above purification process was repeated three times and the ester gave $[\alpha]_D^{31·2°}$ + 12·41° (Patterson gives $[\alpha]_D^{31·2°}$ + 11·60°). The rotation remained unchanged after repetition of the purification process.

Estimation of the acetyl group by the method of Sudborough and Thomas (J., 1905, **87**, 1752) gave 17·2% (Calc.: 17·34) (Found: C, 48·28; H, 6·6. Calc. for $C_{10}H_{16}O_7$: C, 48·37; H, 6·5%). The rotations were taken through a 2-dcm. length, except at the highest temperature for which a 1-dcm. tube was employed. The ester exhibits anomaly; the temperature–rotation curves intersect. Rotations taken above 100° indicated decomposition of the compound.

Densities determined:

$t°$	14·3	34·5	46·5	56·6	90·7	94·5
$d^{t°}_{4°}$	1·1876	1·1676	1·1554	1·1456	1·1118	1·1078

	$d_{4°}^{17·5°}$ = 1·1845.	$d_{4°}^{25·1°}$ = 1·1768.	$d_{4°}^{29·5°}$ = 1·1724.	$d_{4°}^{44·5°}$ = 1·1576.	$d_{4°}^{59·6°}$ = 1·1426.	$d_{4°}^{76·8°}$ = 1·1255.	$d_{4°}^{94·5°}$ = 1·1078.
λ.	$[\alpha]_\lambda^{17·5°}$.	$[\alpha]_\lambda^{25·1°}$.	$[\alpha]_\lambda^{29·5°}$.	$[\alpha]_\lambda^{44·5°}$.	$[\alpha]_\lambda^{59·6°}$.	$[\alpha]_\lambda^{76·8°}$.	$[\alpha]_\lambda^{94·5°}$.
6708	+8·30°	8·61°	8·82°	9·45°	10·08°	10·82°	11·61°
6563	8·62	8·95	9·15	9·79	10·47	11·26	12·09
6438	8·95	9·27	9·48	10·13	10·79	11·62	12·52
6152	9·46	9·84	10·07	10·83	11·59	12·52	13·52
5893	9·82	10·27	10·51	11·41	12·31	13·35	14·46
5590	10·19	10·70	10·99	12·01	13·03	14·23	15·50
5461	10·39	10·90	11·22	12·23	13·30	14·60	15·96
5324	10·46	11·02	11·33	12·47	13·59	14·94	16·40
5086	10·44	11·06	11·44	12·68	13·97	15·48	17·08
4861	10·26	10·95	11·31	12·68	14·11	15·76	17·49
4678	9·85	10·57	10·97	12·46	13·97	15·76	17·67
4455	8·87	9·68	10·12	11·81	13·55	15·61	17·78
4359	8·25	9·12	9·62	11·44	13·29	15·45	17·71

Ethyl Diacetyltartrate.—This ester, prepared by the method of McCrae and Patterson (J., 1900, **77**, 1098), distilled at 163°/10—11 mm. It was fractionated three times and recrystallised from aqueous alcohol five times. Further distillation and recrystallisation caused no change in rotation (Found : C, 49·56; H, 6·29. Calc. for $C_{12}H_{18}O_8$: C, 49·66; H, 6·21%). The compound is anomalous; the temperature–rotation curves intersect. The rotation was found to be slightly higher than the values given by the above authors. Rotations were taken in a 1-dcm. tube.

	$\alpha_D^{67\cdot6°}$.	$[\alpha]_D^{67\cdot6°}$.	M. p.
McCrae and Patterson give	+5·28	4·75	67—68°
The authors find	5·44	4·85	67·7° (corr.)

Densities determined :

$t°$	66	116·1	149·9	182·4
$d_{4°}^{t°}$	1·1149	1·0627	1·0274	0·9934

	$d_{4°}^{74\cdot1°}$ = 1·1059.	$d_{4°}^{87\cdot5°}$ = 1·0920.	$d_{4°}^{101\cdot3°}$ = 1·0779.	$d_{4°}^{122\cdot2°}$ = 1·0562.	$d_{4°}^{142\cdot8°}$ = 1·0350.	$d_{4°}^{162\cdot8°}$ 1·0139.
λ.	$[\alpha]_\lambda^{74\cdot1°}$.	$[\alpha]_\lambda^{87\cdot5°}$.	$[\alpha]_\lambda^{101\cdot3°}$.	$[\alpha]_\lambda^{122\cdot2°}$.	$[\alpha]_\lambda^{142\cdot8°}$.	$[\alpha]_\lambda^{162\cdot8°}$.
6708	+4·67°	5·10°	5·62°	6·58°	7·61°	8·61°
6563	4·78	5·26	5·81	6·80	7·92	8·94
6364	4·93	5·44	6·03	7·12	8·27	9·39
6152	5·04	5·57	6·22	7·43	8·69	9·91
5893	5·13	5·74	6·48	7·80	9·26	10·65
5590	5·08	5·83	6·68	8·20	9·88	11·47
5461	5·01	5·76	6·70	8·36	10·16	11·84
5324	4·85	5·68	6·68	8·44	10·39	12·18
5086	4·29	5·39	6·47	8·44	10·67	12·75
4861	3·51	4·81	6·05	8·23	10·62	13·21
4678	2·64	3·96	5·46	7·92	10·50	13·39
4359	0·09	1·74	3·65	6·76	9·93	13·08

Ethyl Monobenzoyltartrate.—This ester was prepared by a modification of Frankland and McCrae's method (J., 1898, **73**, 307). To 40 g. of anhydrous ethyl tartrate, heated and mechanically stirred in an oil-bath (130—135°), 19 g. of freshly distilled benzoyl chloride were added, drop by drop, during 2 hours. The purification was carried out in accordance with their method, except that anhydrous sodium sulphate was used in place of potassium carbonate as drying agent. The compound was recrystallised four times from light petroleum (b. p. 40—60°); yield 24 g. (Found : C, 57·93; H, 5·87. Calc. for $C_{15}H_{18}O_7$: C, 58·04; H, 5·83%); m. p. 66·2° (corr.); $[\alpha]_D^{24°}$ 19·13°; $[\alpha]_D^{135°}$ 16·68° (compare Frankland and McCrae : yield, 23 g. from 60 g. of ester; m. p. 66—66·5°; $[\alpha]_D^{24°}$ 20·41°; $[\alpha]_D^{135°}$ 16·36°). The ester exhibits anomalous rotatory dispersion, and the temperature–rotation curves for short wave-lengths intersect. Rotations relate to a 1-dcm. column.

Densities determined :

$t°$	28·6	78·0	124·6	161·9	192·0
$d_{4°}^{t°}$	1·1943	1·1489	1·1061	1·0719	1·0424

	$d_{4°}^{28·6°}=$ 1·1943.	$d_{4°}^{49·0°}=$ 1·1754.	$d_{4°}^{67·7°}=$ 1·1582.	$d_{4°}^{85·1°}=$ 1·1423.	$d_{4°}^{103·9°}=$ 1·1251.	$d_{4°}^{124·7°}=$ 1·1060.	$d_{4°}^{142·8°}=$ 1·0891.	$d_{4°}^{160·1°}=$ 1·0734
λ.	$[\alpha]_{\lambda}^{28·6°}$.	$[\alpha]_{\lambda}^{49·0°}$.	$[\alpha]_{\lambda}^{67·7°}$.	$[\alpha]_{\lambda}^{85·1°}$.	$[\alpha]_{\lambda}^{103·9°}$.	$[\alpha]_{\lambda}^{124·7°}$.	$[\alpha]_{\lambda}^{142·8°}$.	$[\alpha]_{\lambda}^{160·1°}$.
6708	+15·52°	15·30°	14·93°	14·62°	14·23°	13·70°	13·29°	12·79°
6563	16·11	15·88	15·50	15·15	14·78	14·25	13·83	13·34
6364	16·90	16·69	16·33	15·95	15·55	15·03	14·61	14·11
6152	17·89	17·63	17·24	16·82	16·43	15·86	15·39	14·90
5893	19·10	18·81	18·42	17·98	17·52	16·94	16·46	15·93
5590	20·57	20·26	19·84	19·43	18·93	18·37	17·85	17·28
5461	21·19	20·87	20·47	20·01	19·53	18·94	18·42	17·82
5324	21·81	21·48	21·06	20·67	20·19	19·57	19·04	18·38
5086	22·68	22·45	22·03	21·66	21·27	20·60	19·95	19·37
4678	23·42	23·43	23·24	22·98	22·62	22·01	21·43	20·67
4472	23·02	23·29	23·33	23·24	23·02	22·47	21·89	21·17
4359	22·48	22·91	23·10	23·18	23·09	22·59	22·03	21·31

Ethyl Dibenzoyltartrate.—This ester was prepared by the method of Frankland and Wharton (J., 1896, **69**, 1583), and after it had stood for a few days in a vacuum desiccator crystals began to form. When crystallisation was almost complete, the mass was dissolved in absolute alcohol, allowed to stand, and then seeded. The major part of the ester then crystallised over-night, and was recrystallised eight times from absolute alcohol (Found: C, 63·80; H, 5·40. Calc. for $C_{22}H_{22}O_8$: C, 63·73; H, 5·36%); m. p. 63·5° (corr.); $[\alpha]_D^{18°}$ − 59·30° (Frankland and Wharton give m. p. 62·5°; $[\alpha]_D^{18°}$ − 59·36°). Its rotatory dispersion is complex and shows minima in the temperature-rotation curves (compare Frankland and Wharton). Rotations were taken in a 1-dcm. column.

Densities determined :

$t°$	16·3	73·95	126·3	158·9	192·9
$d_{4°}^{t°}$	1·1988	1·1498	1·1046	1·0767	1·0477

	$d_{4°}^{16·9°}=$ 1·1984.	$d_{4°}^{26°}=$ 1·1905.	$d_{4°}^{49·5°}=$ 1·1702.	$d_{4°}^{73·2°}=$ 1·1499.	$d_{4°}^{99·4°}=$ 1·1275.	$d_{4°}^{119·1°}=$ 1·1105.	$d_{4°}^{136·8°}=$ 1·0960.	$d_{4°}^{161·4°}=$ 1·0746.
λ.	$[\alpha]_{\lambda}^{16·9°}$.	$[\alpha]_{\lambda}^{26°}$.	$[\alpha]_{\lambda}^{49·5°}$.	$[\alpha]_{\lambda}^{73·2°}$.	$[\alpha]_{\lambda}^{99·4°}$.	$[\alpha]_{\lambda}^{119·1°}$.	$[\alpha]_{\lambda}^{136·8°}$.	$[\alpha]_{\lambda}^{161·4°}$.
6708	−40·97°	−42·50°	−43·69°	−43·57°	−42·33°	−40·63°	−39·34°	−36·49°
6563	43·54	45·11	46·33	46·17	44·73	43·00	41·51	38·70
6438	45·98	47·63	48·82	48·73	47·09	45·21	43·63	40·87
6152	52·21	53·99	55·26	55·00	53·21	51·10	49·24	46·06
5893	58·91	60·81	62·18	61·95	59·82	57·52	55·27	51·94
5590	69·23	71·23	72·75	72·13	69·61	66·67	64·19	60·51
5324	80·16	82·28	83·98	83·22	80·24	76·76	73·91	69·72
5086	93·25	95·51	97·39	95·76	92·24	88·34	84·87	79·76
4861	107·39	109·8	111·86	110·41	106·00	101·10	97·44	91·21
4678	122·40	125·0	127·27	125·10	119·47	114·10	109·40	102·48
4455	144·60	147·4	150·0	146·0	137·70	131·56	125·70	117·74

Ethyl Thionyltartrate.—The most satisfactory method investigated for the preparation of this compound was that given by Schiller (*Ber.*, 1909, **42**, 2017). The following method of purification was adopted The mixture, after reaction, was washed repeatedly with water shaken eight times with 1% sodium carbonate solution, again washed repeatedly with water, dried in ether (anhydrous sodium sulphate) and fractionated in a vacuum. After 9 fractionations, a 3-dcm column of the compound on comparison with a 3-dcm. column of ethyl tartrate, showed practically no colour (Found: C, 37·91 H, 4·72; S, 12·8. Calc. for $C_8H_{12}O_7S$: C, 38·07; H, 4·80; S 12·71%).

The data available for this ester are as follows:

	B. p.		
McKenzie and Barrow (*J.*, *1911*, **99**, *1910*) ...	*160°/12 mm.*	$\alpha_D^{19.5°}$ −244·3°	$[\alpha]_D^{19.5°}$ −183·8°
Schiller (*loc. cit.*)	169°/11·5 mm.		$[\alpha]_D^{17.5-18°}$ −56·71°
Lee (Thesis, University of Birmingham, 1912)	164°/14 mm.	$\alpha_D^{20.3°}$ −241·5°	
Present authors	159°/11 mm.	$\alpha_D^{20.3°}$ −241·36°	$[\alpha]_D^{20.3°}$ −182·56°

On standing, the oil acquires a yellow colour and shows a decrease in rotation. The ester shows simple rotatory dispersion. Rotations at lower temperatures were taken in a 3-dcm. tube, and those at higher temperatures in a 2-dcm. tube. The formula used for calculating [α] at each temperature is given at the foot of the appropriate columns, and the difference (observed—calculated) is shown in the column headed "Diff."

Densities determined:

$t°$	11·8	61·01	106·4	148	174·2
$d_{4°}^{t°}$	1·3320	1·2749	1·2225	1·1738	1·1423

	$d_{4°}^{13.1°}$ = 1·3305.		$d_{4°}^{20.3°}$ = 1·3221.		$d_{4°}^{42.3°}$ = 1·2966.	
λ.	$[\alpha]_\lambda^{13.1°}$.	Diff.	$[\alpha]_\lambda^{20.3°}$.	Diff.	$[\alpha]_\lambda^{42.3°}$.	Diff.
6869·5	−130·85°	−0·01	−129·45°	+0·01	−126·27°	+0·01
6708			136·48	+0·04		
6563	144·79	+0·02	143·21	−0·01	139·69	−0·01
6364			153·40	−0·01		
6152	167·31	+0·02	165·54	−0·03	161·49	−0·01
5893	184·42	±0	182·56	±0	178·07	−0·02
5590	208·26	+0·05	206·22	+0·03	201·16	+0·02
5461			217·70	−0·02		
5324			231·22	+0·09	225·54	+0·06
5086	260·08	+0·01	257·73	−0·02	251·40	−0·05
4861	290·11	−0·01	287·63	−0·05	280·59	−0·06
4678	318·91	+0·06	316·29	−0·01	308·55	−0·04
4472	357·15	+0·10	354·45	−0·13	345·80	+0·03
4359	381·20	−0·03	378·56	+0·04	369·30	−0·03

$[\alpha]_\lambda^{13.1°} = -\frac{56.183}{\lambda^2 - 0.042642}$ $[\alpha]_\lambda^{20.3°} = -\frac{55.46}{\lambda^2 - 0.043495}$ $[\alpha]_\lambda^{42.3°} = -\frac{54.089}{\lambda^2 - 0.43556}$

$d_{4°}^{56·9°} = 1·2796$. $d_{4°}^{92·8°} = 1·2496$. $d_{4°}^{106·9°} = 1·2216$.

λ.	$[\alpha]_\lambda^{56·9°}$.	Diff.	$[\alpha]_\lambda^{92·8°}$.	Diff.	$[\alpha]_\lambda^{106·9°}$.	Diff.
6869·5	−124·43°	+0·03	−121·54°	±0	−119·52°	+0·01
6708						
6563	137·66	+0·02	134·42	−0·09	132·27	+0·00
6364			144·17	+0·06		
6152	159·09	−0·01	155·51	−0·05	152·94	−0·03
5893	175·42	±0	171·55	−0·03	168·71	−0·02
5590	198·14	+0·04	193·88	+0·01	190·66	+0·02
5461						
5324	222·14	+0·10	217·47	+0·05	213·88	+0·08
5086	247·66	+0·08	242·52	−0·05	238·51	−0·03
4861	276·28	−0·01	270·89	−0·03	266·34	−0·04
4678	303·77	+0·03			293·05	+0·01
4472	340·40	−0·12	334·09	−0·01	328·66	+0·09
4359	363·40	+0·01	357·00	−0·01	351·10	−0·01

$[\alpha]_\lambda^{56·9°} = -\dfrac{53·331}{\lambda^2 - 0·04326}$ $[\alpha]_\lambda^{92·8°} = -\dfrac{51·955}{\lambda^2 - 0·04448}$ $[\alpha]_\lambda^{106·9°} = -\dfrac{51·083}{\lambda^2 - 0·04452}$

$d_{4°}^{125·2°} = 1·2003$. $d_{4°}^{145·4°} = 1·1768$.

λ.	$[\alpha]_\lambda^{125·2°}$.	Diff.	$[\alpha]_\lambda^{145·4°}$.	Diff.
6869·5	−118·27°	±0	−117·28°	+0·03
6708			123·63	+0·04
6563	130·89	−0·01	129·72	±0
6364			138·95	±0
6152	151·40	−0·03	149·95	+0·01
5893	166·94	−0·03	165·33	+0·01
5590	188·65	+0·01	186·76	+0·07
5461			197·12	±0
5324	211·60	+0·04	209·34	+0·10
5086	235·98	−0·05	233·28	−0·03
4861	263·51	−0·05	260·34	−0·01
4678	289·87	−0·06	286·21	±0
4472	325·12	−0·06	320·72	+0·11
4359	347·38	−0·03	342·30	−0·11

$[\alpha]_\lambda^{125·2°} = -\dfrac{50·564}{\lambda^2 - 0·04444}$ $[\alpha]_\lambda^{145·4°} = -\dfrac{50·275}{\lambda^2 - 0·04318}$

At 149° a decrease of rotation $\alpha_{5086} = 0·03°$ was noted.

Ethyl-Dichlorosuccinate.—This ester was prepared by the method given by Lee (*loc. cit.*) from the ethyl thionyl ester, using pyridine hydrochloride as a catalyst (1 mol. thionyl ester, freshly prepared; 1 mol. thionyl chloride; and 2 mols. pyridine hydrochloride; heated together for 8 hours on a water-bath at 100°). The resulting oil was washed repeatedly with water, taken up in ether, dried over sodium sulphate, and fractionated in a vacuum eight times; b. p. 128°/12—13 mm.; $\alpha_D^{20°}$ − 52·54° (Found: Cl, 28·7. Calc. for $C_8H_{12}O_4Cl_2$: Cl, 29·18%). On standing, racemisation or loss of hydrogen chloride takes place and the rotation decreases; the ester cannot then be brought up to its original rotation by vacuum fractionation. The ester shows simple rotatory dispersion. Rotations were taken in a 2-dcm. tube.

Densities determined :

$t°$	9·1	61·4	110·6	148·4
$d_{4°}^{t°}$	1·2495	1·1902	1·1346	1·0908

$d_{4°}^{12·7°} = 1·2454$. $d_{4°}^{22·6°} = 1·2343$. $d_{4°}^{41·4°} = 1·2130$.

λ.	$[\alpha]_\lambda^{12·7°}$.	Diff.	$[\alpha]_\lambda^{22·6°}$.	Diff.	$[\alpha]_\lambda^{41·4°}$.	Diff.
6869·5	−29·89°	+0·01	−29·97°	±0	−30·02°	+0·01
6708	31·54	+0·02	31·62	±0	31·75	+0·09
6563	33·12	+0·01	33·23	+0·02	33·26	±0
6364	35·52	+0·01	35·50	−0·03	35·60	+0·02
6152	38·36	−0·02	38·47	−0·02	38·53	−0·02
5893	42·40	−0·01	42·52	±0	42·58	−0·02
5590	48·02	−0·01	48·24	+0·09	48·29	+0·06
5461	50·77	−0·02	50·87	−0·04	51·01	+0·01
5324	54·00	±0	54·11	−0·02	54·27	+0·05
5086	60·39	−0·02	60·51	−0·03	60·66	±0
4861	67·64	−0·03	67·78	−0·01	67·91	−0·03
4678	74·62	−0·04	74·75	−0·03	74·97	+0·02
4472	84·04	+0·01	84·12	−0·03	84·37	+0·02
4359	90·02	±0	90·14	+0·02	90·36	±0

$[\alpha]_\lambda^{12·7°} = -\dfrac{12·611}{\lambda^2 - 0·04992}$ $[\alpha]_\lambda^{22·6°} = -\dfrac{12·663}{\lambda^2 - 0·04950}$ $[\alpha]_\lambda^{41·4°} = -\dfrac{12·67}{\lambda^2 - 0·04979}$

$d_{4°}^{62·4°} = 1·1892$. $d_{4°}^{87°} = 1·1613$. $d_{4°}^{104·1°} = 1·1420$.

λ.	$[\alpha]_\lambda^{62·4°}$.	Diff.	$[\alpha]_\lambda^{87°}$.	Diff.	$[\alpha]_\lambda^{104·1°}$.	Diff.
6869·5	−29·63°	−0·01	−28·84°	−0·01	−28·26°	+0·01
6708	31·26	−0·01	30·46	+0·02	29·83	+0·02
6563	32·84	−0·01	31·98	±0	31·34	+0·01
6364	35·20	−0·02	34·31	±0	33·62	+0·01
6152	38·04	−0·03	37·15	+0·06	36·34	±0
5893	42·05	−0·01	41·01	+0·01	40·17	±0
5590	47·74	+0·10	46·48	+0·01	45·55	+0·03
5461	50·35	−0·02	49·16	+0·01	48·16	±0
5324	53·57	+0·01	52·30	+0·02	51·25	+0·02
5086	59·90	−0·02	58·53	±0	57·39	+0·03
4861	67·11	±0	65·61	−0·01	64·34	+0·02
4678	74·05	+0·01	72·46	±0	71·03	±0·00
4472	83·36	+0·02	81·68	+0·03	80·07	±0·00
4359	89·31	+0·03	87·53	±0	85·81	−0·03

$[\alpha]_\lambda^{62·4°} = -\dfrac{12·508}{\lambda^2 - 0·04991}$ $[\alpha]_\lambda^{87°} = -\dfrac{12·131}{\lambda^2 - 0·05141}$ $[\alpha]_\lambda^{104·1°} = -\dfrac{11·876}{\lambda^2 - 0·05165}$

At 122·9° an increase of rotation $\alpha_{5154} = 0·33°$ was noted, which indicated decomposition, and comparison of observed with calculated values showed *the rotatory dispersion still to be simple.*

Methyl Tartrate.—This ester was prepared from Kahlbaum's methyl alcohol by the continuous esterification process mentioned under ethyl tartrate (150 g. tartaric acid; 14 hrs.; oil-bath at 120—125°). It was fractionated in vacuum six times, and had b. p. 165—166°/11·5 mm., m. p. 48°. Rotations were taken in a 2-dcm. tube.

Densities determined :

$t°$	29·5	53·3	67·8	88·3	122·9	138·9	170
$d_{4°}^{t°}$	[illegible]	[illegible]	1·2836	1·2824	1·2263	1·2093	1·1770

λ.	$d_{4°}^{17·7°}$ (extrapolated) = 1·3356. $[\alpha]_{\lambda}^{17·7°}$.	$d_{4°}^{34·9°}$ = 1·3180. $[\alpha]_{\lambda}^{34·9°}$.	$d_{4°}^{58·8°}$ = 1·2921. $[\alpha]_{\lambda}^{58·8°}$.
6708	+2·32°	3·45°	4·53°
6563	2·36	3·49	4·62
6438	2·34	3·49	4·67
6152	2·19	3·45	4·75
5893	1·87	3·28	4·73
5590	1·21	2·84	4·56
4359	−9·17	−5·81	−2·24

λ.	$d_{4°}^{81·2°}$ = 1·2698. $[\alpha]_{\lambda}^{81·2°}$.	$d_{4°}^{95·3°}$ = 1·2549. $[\alpha]_{\lambda}^{95·3°}$.	$d_{4°}^{100·8°}$ = 1·2495. $[\alpha]_{\lambda}^{100·8°}$.	$d_{4°}^{124·9°}$ = 1·2246. $[\alpha]_{\lambda}^{124·9°}$.	$d_{4°}^{144·8°}$ = 1·2033. $[\alpha]_{\lambda}^{144·8°}$.	$d_{4°}^{162·1°}$ = 1·1853. $[\alpha]_{\lambda}^{162·1°}$.
6708	+5·18°	5·54°	5·67°	6·08°	6·33°	6·51°
6152	5·57	6·02	6·21	6·79	7·18	7·43
5893	5·68	6·16	6·36	7·02	7·52	7·87
5590	5·62	6·21	6·43	7·22	7·75	8·15
5324	5·38	5·99	6·30	7·16	7·74	8·15
5086		5·55		6·86	7·59	8·05
4359	−0·02	1·21	1·65	3·40	4·55	

Methyl Monoacetyltartrate.—The ester was prepared similarly to the ethyl analogue, and purified as follows: The benzene was removed and the residual oil shaken with 5 c.c. of water and separated. This was repeated twice. The oil was then dissolved in a large volume of water and cooled to 0°; the diacetyltartrate which separated was filtered off, the filtrate extracted with ether, the extract dehydrated over sodium sulphate, the solvent removed, and the residual monoacetyl ester crystallised from benzene to constant rotation and m. p., 82·4°. Estimation of acetyl group by Sudborough and Thomas's method (*loc. cit.*) gave 19·3 (Calc., 19·54%) (Found: C, 43·55; H, 5·6. Calc. for $C_8H_{12}O_7$: C, 43·62; H, 5·49%). Rotations were taken in 1-dcm. tube. The ester exhibits anomalous rotatory dispersion.

Densities determined:

$t°$	87·2	100·5	132	144·5
$d_{4°}^{t°}$	1·2131	1·1987	1·1639	1·1503

λ.	$d_{4°}^{85·2°}$ = 1·2156.* $[\alpha]_{\lambda}^{85·2°}$.	$d_{4°}^{105·4°}$ = 1·1931. $[\alpha]_{\lambda}^{105·4°}$.	$d_{4°}^{124·4°}$ = 1·1724. $[\alpha]_{\lambda}^{124·4°}$.	$d_{4°}^{140·8°}$ = 1·1546. $[\alpha]_{\lambda}^{140·8°}$.
6708	+2·06°	3·19°	3·88°	4·19°
6563	2·04	3·25	3·99	4·38
6438	2·02	3·32	4·09	4·53
6152	1·94	3·37	4·28	4·81
5893	1·80	3·35	4·39	5·00
5590	1·54	3·23	4·38	5·11
5461	1·39	3·12	4·32	5·10
5324	1·15	2·95	4·23	5·08
5086	0·51	2·50	3·96	4·94
4861	−0·33	1·90	3·51	4·59
4678	−1·14	1·27	2·99	4·20
4455	−2·21	0·35	2·26	3·53
4359	−2·80	−0·05	1·86	3·21

* Extrapolated.

Methyl Diacetyltartrate.—The ester was prepared by heating methyl tartrate and acetic anhydride for 3 hours and finally raising it to its boiling point. The excess of acetic anhydride was removed under reduced pressure and the residue poured into water. The compound was purified by vacuum distillation and recrystallisation from aqueous alcohol; m. p. 106·5°; $\alpha_D^{107\cdot3^\circ}$ − 9·01° (Found: C, 45·65; H, 5·23. Calc. for $C_{10}H_{14}O_8$: C, 45·8; H, 5·38%). Freundler (*Compt. rend.*, 1892, **115**, 509; *Bull. Soc. chim.*, 1894, [3], **11**, 305) gave m. p. 103° and determined the rotation in alcoholic solution. The dispersion curves are complex and anomalous; crossing of the zero axis takes place towards the red end of the spectrum for the highest temperature. Rotations were taken in a 1-dcm. tube.

Densities determined :

t°	113	134·1	143·5	157	181
$d_{4^\circ}^{t^\circ}$	1·1407	1·1150	1·1034	1·0868	1·0575

	$d_{4^\circ}^{107\cdot3^\circ}$ = 1·1480.*	$d_{4^\circ}^{128\cdot3^\circ}$ = 1·1220.	$d_{4^\circ}^{143\cdot3^\circ}$ = 1·1036.	$d_{4^\circ}^{171\cdot5^\circ}$ = 1·0689.	$d_{4^\circ}^{178\cdot3^\circ}$ = 1·0609.
λ.	$[\alpha]_\lambda^{107\cdot3^\circ}$.	$[\alpha]_\lambda^{128\cdot3^\circ}$.	$[\alpha]_\lambda^{143\cdot3^\circ}$.	$[\alpha]_\lambda^{171\cdot5^\circ}$.	$[\alpha]_\lambda^{178\cdot3^\circ}$.
6708	−5·20°	−3·96°	−2·85°	−0·12°	+0·75°
6563	5·53	4·27	3·06	0·19	+0·70
6463	5·87	4·54	3·28	0·23	+0·59
6152	6·83	5·35	3·91	0·52	+0·39
5893	7·85	6·22	4·65	0·84	+0·10
5590	9·32	7·41	5·72	1·64	−0·56
5324	11·14	8·89	6·98	2·48	−1·24
5086	13·21	10·62	8·42	3·46	−2·16
4861	15·83	12·75	10·06	4·74	−3·33
4678	18·21	14·85	11·92	6·10	−4·57
4455	21·67	17·99			−6·76

* Extrapolated.

Methyl Monobenzoyltartrate.—This was prepared by slowly adding benzoyl chloride (1 equiv.) to a stirred mixture of methyl tartrate and petroleum ether (b. p. 60—80°), the mixture then being boiled under reflux for 5 days. The petroleum ether was decanted and the layer of residual oil dissolved in benzene, treated with sodium carbonate solution, washed with water, dried over anhydrous sodium sulphate, and the benzene removed. The oil thus obtained was extracted with hot water and the solution filtered. The cold aqueous solution of the required ester was then extracted with ether, and when the latter was removed, the product solidified and was recrystallised from benzene; m. p. 78° (Found: C, 55·22; H, 4·8. Calc. for $C_{13}H_{14}O_7$: C, 55·3; H, 4·99%). Rotations were taken in a 1-dcm. tube. The ester exhibits anomalous rotatory dispersion.

Densities determined :

t°	50·5	79·6	93·5	127·4	146·1	158
$d_{4^{\circ}}^{t^{\circ}}$	*1·2487*	*1·2204*	*1·2065*	*1·1729*	*1·1533*	*1·1418*

	$d_{4^{\circ}}^{22^{\circ}}=$ 1·2780.	$d_{4^{\circ}}^{57^{\circ}}=$ 1·2430.	$d_{4^{\circ}}^{80·8^{\circ}}=$ 1·2102.	$d_{4^{\circ}}^{125·3^{\circ}}=$ 1·1744.	$d_{4^{\circ}}^{157^{\circ}}=$ 1·1427.
λ.	$[\alpha]_{\lambda}^{22^{\circ}}$.	$[\alpha]_{\lambda}^{57^{\circ}}$.	$[\alpha]_{\lambda}^{80·8^{\circ}}$.	$[\alpha]_{\lambda}^{125·3^{\circ}}$.	$[\alpha]_{\lambda}^{157^{\circ}}$.
6708	+4·13°	4·63°	4·99°	4·91°	4·90°
6563	4·13	4·73	5·09	5·06	5·05
6438	4·10	4·80	5·18	5·18	5·16
6152	4·01	4·87	5·27	5·35	5·36
5893	3·85	4·78	5·21	5·40	5·44
5589	*3·51*	*4·51*	*5·00*	*5·40*	*5·45*
5461	3·30	4·33	4·84	5·30	5·37
5324	2·93	4·06	4·65	5·14	5·22
5086	1·85	3·15	3·91	4·56	4·73
4861	0·41	2·01	2·80	3·67	4·03
4678	−1·05	0·48	1·31	2·63	3·19
4455	−3·46	−1·65	−0·60	1·04	1·91
4359	−4·38	−2·48	−1·40	0·20	1·21

Methyl Dibenzoyltartrate.—This was prepared by the method described by Frankland and Wharton (J., 1896, **69**, 1583). (Found : C, 62·1; H, 4·78: Calc. for $C_{20}H_{18}O_8$: C, 62·15; H, 4·7%). *Comparative data are :*

	Frankland and Wharton.	Present authors.
M. p.	135·5°	135·5°
$d_{4^{\circ}}^{150^{\circ}}$	1·1285	1·1306
$d_{4^{\circ}}^{160^{\circ}}$	1·1191	1·1223
$[\alpha]_{D}^{137^{\circ}}$	−66·84°	−64·2°

Rotations were taken in a 1-dcm. tube. The ester exhibits complex rotatory dispersion.

Densities determined :

t°	140·6	153·7	166·2
$d_{4^{\circ}}^{t^{\circ}}$	1·1384	1·1276	1·1171

	$d_{4^{\circ}}^{135·4^{\circ}}=$ 1·1428.	$d_{4^{\circ}}^{152·6^{\circ}}=$ 1·1285.
λ.	$[\alpha]_{\lambda}^{135·4^{\circ}}$.	$[\alpha]_{\lambda}^{152·6^{\circ}}$.
6708	−45·78°	−43·03°
6563	48·23	45·51
6438	50·88	47·78
6152	57·42	53·95
5893	64·51	60·59
5590	74·69	69·95
5461	79·96	74·79
5324	85·76	80·34
5086	97·95	91·57
4861	112·18	104·60
4678	126·13	118·01
4455	145·68	137·88
4359	153·5	147·11

Summary.

(1) Inflexion and maxima are confined to the positive region of rotation, and crossing of the axis, $d\alpha/d\lambda$, is positive for methyl and

ethyl *d*-tartrates and those derivatives of the two esters which exhibit anomalous rotatory dispersion.

(2) The occurrence of anomalous rotatory dispersion is an indication of the relative configuration.

(3) The explanation of anomaly by consideration of ultra-violet terms only is incomplete. A view has been put forward postulating an infra-red term in the Drude equation. The term is negative for a compound of relative configuration "*d*." This term, though its contribution may be small compared with rotation of electronic origin, is necessary, for it controls (*a*) the association of the high-frequency constant with the positive ultra-violet term, and (*b*) the final course of the path to the infra-red band in the positive region.

(4) The consideration of anomaly involves both the superposition rule (Lowry, *loc. cit.*), and also Wood's interpretation of Drude's view of spurious anomaly; for the dispersion occurs between two bands, the low-frequency band in the ultra-violet, and the infra-red band, and not merely outside the ultra-violet bands (longer wave-length side), the infra-red band being neglected.

(5) Quartz is taken as an illustration of the importance of the infra-red term.

(6) By an extension of Thomson's view, a single asymmetric centre can give rise to anomaly.

(7) Different classes of anomalous rotatory dispersion are discussed.

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CCXX.—*Rotatory Dispersion: Intersections of Dispersion Curves and of Temperature–Rotation Curves.*

By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS.

IT is well known that the temperature–rotation curves for methyl, ethyl, propyl, butyl, heptyl, and octyl *d*-tartrates show maxima in the positive region of rotation and that such maxima are displaced to a higher temperature with decrease of wave-length. The

esters thus exhibit similar phenomena (Patterson, J., 1916, **109**, 1139, etc.: Frankland and Garner, J., 1919, **115**, 636; Winther, *Z. physikal. Chem.*, 1902, **41**, 161; Walden, *Ber.*, 1905, **38**, 366). A maximum in a temperature–rotation curve for a particular wave-length corresponds to the particular wave-length point on a dispersion curve, this point being situated vertically above points for the same wave-length on all other dispersion curves both for lower and higher temperatures.

Under certain conditions a maximum is defined by the point of intersection of two dispersion curves, the wave-length corresponding to the point of intersection having maximum rotation between the limits of temperature of the two dispersion curves—the closer the temperature limits, the more accurately is the maximum rotation defined for the wave-length of intersection. In general, maxima in temperature–rotation curves indicate intersection in dispersion curves except in cases of simplicity. The movement of maxima is indicated by a particular type of intersection.

Manner of Intersection of Dispersion Curves showing Maxima of Positive Rotation.—Intersections of the dispersion curves occur in a definite order. The diagrammatic dispersion curves (Fig. 1) represent maxima of rotation for different wave-lengths and their movement in the positive region. The lower-temperature dispersion curve (for 60°) is cut by the steeper higher-temperature curve (for 80°) at λ_1. The intersection indicates (i) a maximum in the temperature–rotation curves for λ_1, (ii) maxima for all wave-lengths greater than λ_1, more pronounced definition of the maxima occurring the greater the wave-length, and (iii) no maxima for all wave-lengths less than λ_1, less pronounced approach to maxima occurring the smaller the wave-length. Therefore the maxima for different wave-lengths are moving into the blue region of the spectrum with increase of temperature. The important point to note is that decrease of rotation causing maxima originates in the red. The movement of maxima is shown clearly when the higher-temperature dispersion curve cuts the lower and becomes the dispersion curve of ***highest rotational value*** towards the blue.* This intersection depends upon a relatively large temperature rotation movement of the maxima, or if small, the experimental determination of dispersion curves of only small temperature differences in the region of intersection.

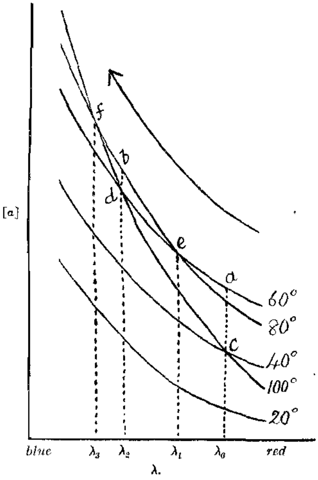
The steepest (100°) dispersion curve cuts the lower-temperature curves in the following order: 40°, 60°, 80°, and finally becomes the curve of highest rotational value in the blue, *i.e.*, on decreasing

* Secondary intersections (as *c*, *d*, Fig. 1) indicate also the type of intersection.

the wave-length the dispersion curve for 100° intersects other dispersion curves in the order of increasing temperature, and thus at the intersection of the 100° and 80° curves the maximum rotation is carried to a higher temperature in the blue.

This order of intersection and origination of maxima in the red occurs in those derivatives of *d*-tartaric and *l*-lactic acids which show movements of maximum rotation for different wave-lengths

Fig. 1.



in the positive region. If the following condition obtained—that the 100° curve intersected the dispersion curves in the irregular order, 40°, 80°, 60°—a discontinuity would be noted resulting in an irregularity, a depression, in the temperature–rotation curves.

The values *e* and *f* may be regarded as the maximum rotations attained by the wave-lengths λ_1 and λ_3, respectively, under the experimental conditions investigated. Similarly the values for *a* and *b* may be regarded as maxima. The secondary intersection *c* (intersection of dispersion curves for wider temperature limits than the primary intersection) gives two equal rotational values, one for

40° on one side, and the other for 100° on the other side, of the maximum rotation a for λ_0.

Curve of Maximum Dispersion.—The curve *fba* into the red region is an infinite number of intersecting dispersion curves which intersect systematically (without irregularity of the type of intersection, the intersections passing gradually out of the red into the blue region) and give rise to a curve of maximum dispersion developing in the direction red–blue (Fig. 1). The curve will lie just above a primary intersection, and will coincide with the two intersecting curves, *viz.*, the low-temperature dispersion curve on the side of the intersection directed towards the red, and the high-temperature curve on the side directed towards the blue. This curve is interesting, for it has direction and shows clearly the variation of maximum rotation with change of wave-length. Further the generation of this curve, *i.e.*, the type of intersection, shows how dispersion curves pass over the maximum of a surface into a non-anomalous region where increase of temperature causes a decrease of rotation and where there is no access to the negative region with decrease of rotation. The only way of gaining the zero axis is by a passage back over the maximum into the anomalous region.

Intersection of Dispersion Curves.

Ethyl Tartrate.—The intersections of the α–λ dispersion curves * for ethyl tartrate have been studied and the measurements are given below.

λ.	Temp. 120°.	140°.	152°.	162·4°.	173°.
7214	+11·87	11·94	11·90	11·82	11·71
7006	12·14	12·20	12·15	12·08	11·99
6707	12·85	12·97	12·94	12·88	12·78
6364		14·10	14·10	14·05	13·96
6152		14·83	14·85	14·82	14·73
5833		*15·86*	*15·92*	*15·90*	*15·82*
5590		17·08	17·16	17·15	17·08
5461		17·63	17·71	17·72	17·66
5219			18·75	18·82	18·78
5154				19·11	19·13
5086				19·39	19·43
4964				19·89	19·95

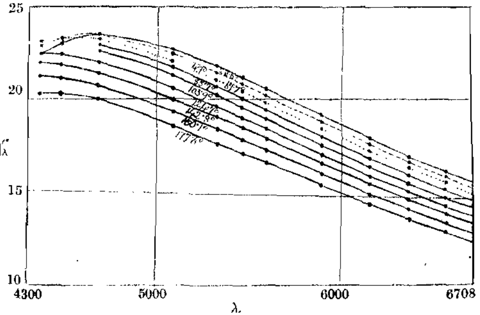
(The rotations were taken in a 3-dcm. tube. Densities determined: $d_{4°}^{149·9°}$ 1·0720; $d_{4°}^{181·3°}$ 1·0386.)

* The authors recognise that the returning of the a–λ dispersion curves is open to criticism. To obtain intersection of the $[a]$–λ curves, it is necessary to work at over 200° (compare Patterson, *loc. cit.*), which is difficult. They have not observed change in the mode of intersection of the a–λ dispersion curves to that present in the final $[a]$–λ curves in any compound yet examined; it is a good guide to the probability of intersection of the $[a]$–λ curves at higher temperatures.

From the above measurements the 152° dispersion curve intersects the 140° curve at $\lambda = 6364$; the 162·4° curve intersects the 140° curve at about $\lambda = 6152$ and the 152° curve between λ 5590 and λ 5461; finally, the 173° curve intersects the 140° curve at $\lambda = 5590$, the 152° curve between $\lambda = 5461$ and λ 5219, and the 162·4° curve between λ 5219 and 5154, becoming the dispersion curve of highest rotational value towards the blue. A curve of *maximum dispersion* (α, λ) *originating in the red* can be drawn touching the family of curves, which curve may be looked upon as an envelope of the family.

Ethyl Monobenzoyltartrate.—The dispersion curves (Fig. 2*a*) of this derivative are interesting. They are remarkably parallel and

FIG. 2*a*.



Rotatory dispersion curves for ethyl monobenzoyltartrate.

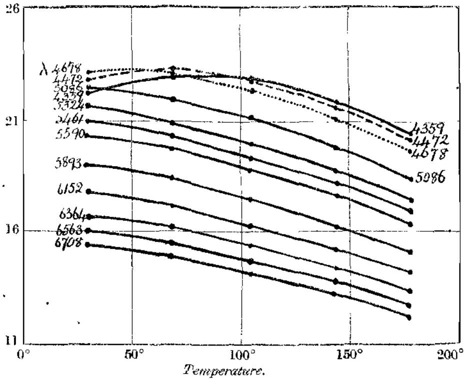
show maxima for the low temperatures, but only approaches to maxima for the high temperatures. Intersections taking place in the blue and the violet in the usual manner give rise to the maxima as shown in the temperature–rotation diagram (Fig. 2*b*) (Wood and Nicholas, this vol., p. 1671).

These dispersion curves lie almost wholly (except those for wave-lengths in the blue and violet for the lower temperatures) on a descending surface, where increase of temperature, though decreasing the rotation, removes them from the region of anomaly. The temperature–rotation curves make this point clear, for they (λ 5086—λ 6708) are on a surface to the right of the maxima; a point of importance is that to the right of the maxima the curves show no tendency to converge and intersect. Curves for tem-

peratures higher than 160·1° may not be trustworthy owing to slight decomposition in the compound, but up to 190° there was no indication of minima (see curve for 177·6°).

Frequently in experimental work intersecting dispersion curves are obtained as represented diagrammatically in Fig. 3. From a consideration of these curves it is clear that the temperature–rotation curves show no definite movement of the maxima with temperature, maxima for all wave-lengths being situated apparently at 80°; nevertheless, the higher-temperature dispersion curve is the steepest, the inference being that the maxima for different

FIG. 2b.



*Rotation–temperature curves for ethyl monobenzoyl-*d*-tartrate.*

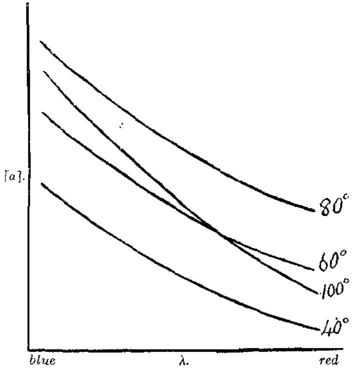
wave-lengths exhibit small movement in the neighbourhood of 80° to a higher temperature and higher rotation as the wave-length decreases. The range of temperature for investigating the movement of maxima has not been selected appropriately. It may so happen that the 100° dispersion curve is coincident or almost coincident with the 80° curve, definite intersection being within experimental error. This is owing to the parallelism of the dispersion curves.

A Dispersion–Temperature Relationship for Two Enantiomorphs.

Ethyl *d*-tartrate is anomalous in the positive region. Its dispersion curves show crossing of the axis in a definite manner, maxima,

inflexion, and intersection of a particular type. Its temperature–rotation curves show crossing of the axis ($d\alpha/dT$ positive), intersection, and maxima of positive rotation moving in the manner indicated above. With the exception of the passage of curves from the negative to the positive region of rotation, these characteristics occur only in the positive region. It is inferred that such characteristics are definite criteria for a compound of *d*-configuration. For instance none of the *n*-alkyl *l*-lactates (methyl to nonyl inclusive) exhibits visible anomaly in the homogeneous condition, but certain of the esters (including *iso*butyl *l*-lactate)

FIG. 3.



show definite movement of maxima (temperature–rotation curves) to a higher temperature with decreasing wave-length.

l-α-Naphthylmethylcarbinol (Pickard and Kenyon, J., *1914*, **105**, 1115) is anomalous in the negative region of rotation, and its temperature–rotation curves exhibit movement of maxima to a higher temperature with decreasing wave-length. Since the intersection of its dispersion curves takes place in the negative region and is of similar general character to the method of intersection of the dispersion curves of ethyl *d*-tartrate situated in the positive region, it is inferred that the alcohol exhibits *maxima* of negative rotation and is related configuratively to *l*-tartaric acid. If temperature–rotation curves showing maxima and their movement be drawn diagrammatically for a compound of *d*-configuration, then

the maxima and their movement for a compound of *l*-configuration may be represented by a mirror image situated in the negative region. This method of ascertaining the configuration of a compound by maxima of positive or negative rotation is dependent on the following conditions: (1) The crossing of the axis, $d\alpha/dT$, is positive for a compound of *d*-configuration and negative for a compound of *l*-configuration on the temperature–rotation diagram, provided that the maxima are to the right of the region of anomaly; (2) maxima move in the manner indicated, provided that the region of anomaly is to the left of the maxima. If the region of anomaly is to the right of the maxima, then crossing of the axis $d\alpha/dT$ is negative (compound of *d*-configuration) or positive (compound of *l*-configuration). The maxima will move to a lower temperature with decrease in wave-length. This follows from the convention of plotting temperature in one direction only, without reference to the singular way of crossing the axis in the dispersion diagram. [Compare the esters of *d*-benzylmethylcarbinol (Kenyon and Pickard, J., 1914, **105**, 2271), in which increase of temperature causes a decrease in rotation.]

"*Negative*" *Minima*.

The temperature–rotation curves to be considered are situated in the negative region and are concave towards the axis of zero rotation. In these respects they are similar to the temperature–rotation curves showing maxima of negative rotation (compound of *l*-configuration). The former for sodium light were first investigated by Frankland and Wharton (J., 1896, **69**, 1587) and the curve obtained for ethyl dibenzoyl-*d*-tartrate was described as "the passage through a maximum in the change of rotation brought about by change of temperature." Patterson (*loc. cit.*), however, describes such curves as showing minima of rotation, rotation being considered in an absolute sense. They are considered here as true minima and are termed "negative" minima.

The dispersion diagram for ethyl dibenzoyl-*d*-tartrate exhibits the following main features: (1) Increase of temperature increases the rotation until a definite temperature is reached, after which further increase of temperature decreases the rotation; (2) dispersion curves intersecting in the order of increasing temperatures; (3) a curve of minimum dispersion originating, in the visible spectrum, in the violet. The minima in temperature–rotation curves therefore move to a lower temperature with decrease of wave-length.

A number of unrecorded intersecting dispersion curves were obtained for this compound—one curve had rotation $[\alpha]_{6708}^{68\cdot9^\circ} = -43\cdot71^\circ$ and $[\alpha]_{4678}^{68\cdot9^\circ} = -126\cdot85^\circ$ (compare experimental portion

of preceding paper)—all of which definitely exhibited the movement These results are in agreement with the investigation of Patterson on *iso*butyl dibenzoyl-*d*-tartrate.(*Proc. Roy. Soc. Edin.*, 1918, **39** 18).

The movement of negative minima (compound of *d*-configuration is in a direction opposite to the movement of maxima of negative rotation (compound of *l*-configuration). This movement holds for those minima which have been investigated. Cases may arise where it is not easy to distinguish negative minima from maxima of negative rotation. It has been mentioned that maxima move in one direction only provided that such maxima are plotted on the temperature–rotation diagram to the right of the crossing of the axis and region of anomaly. If minima are plotted to the left of the crossing of the axis, $d\alpha/dT$ positive, only then is it possible to distinguish clearly negative minima by their movement from maxima of negative rotation (in absence of anomaly) and hence the configuration of the compound.

Considering minima, it is necessary to ascertain that no intersection of the temperature–rotation curves occurs in the negative region, and further, that crossing of the axis and region of anomaly, provided these points can be investigated accurately by extrapolation, are to the right of the plotted curves in the temperature-rotation diagram. Considerable information on these points is given by a characteristic diagram (Patterson, J., 1916, **109**, 1139) An important point with regard to compounds showing negative minima is that, although solvents alter the rotation to some extent yet the effect is not great, and in certain solvents the minima persist (Patterson, *Proc. Roy. Soc. Edin.*, 1918, **39**, 18), which is not the case, as a rule, with compounds exhibiting maxima.

The fourth case—positive minima (compound of *l*-configuration)—situated in the positive region of rotation, has not been investigated so far as we are aware. This case may be looked upon as being in general character, a mirror image of the minima discussed. further, it is assumed that the occurrence and movement of minima is a dispersion–temperature relationship for two enantiomorphs, and that such movement differentiates them from maxima.

In illustration of a few points as to the nature of the region from minima to crossing of the axis, the results obtained from the investigation of methyl diacetyl-*d*-tartrate may be mentioned. The dispersion curves lie in the negative region except for the highest temperature, when crossing of the zero axis occurs. The temperature–rotation curves show approach to minima, convergence on proceeding towards the axis but no intersection, and crossing of the axis to the right of the probable minima for the

curves of longer wave-length. Since anomaly is in the positive region and crossing of the axis ($d\alpha/dT$) is positive, it is inferred that the temperature–rotation curves are approaching to negative minima of a similar type to those exhibited by ethyl dibenzoyl-tartrate. Had the compound possessed the reverse temperature coefficient with regard to rotation, the temperature–rotation curves would cross the axis to the left of the minima; it is necessary, therefore, to consider the region of anomaly or other characteristics mentioned.

Ethyl *d*-dichlorosuccinate exhibits simple rotatory dispersion in the visible spectrum and negative minima in the temperature–rotation curves. Definite indication of movement of the minima could not be obtained owing to the remarkable parallelism of the dispersion curves. If the movement of minima occurs, it is over a very close range of temperature and is within experimental error. In this connexion it is interesting to note that ethyl dibenzoyl-*d*-tartrate is complex.

Minima of Positive Rotation.

*iso*Butyl diacetyl-*d*-tartrate, investigated by Patterson (*loc. cit.*), shows minima of positive rotation which move to a higher temperature and lower rotation with increase of wave-length. Intersection and consequent development of a dispersion enveloping curve of minimum rotation in the direction violet ⟶ red occurs, which is characteristic of those *d*-tartrates which show negative minima and movement of minima in the negative region.

It is assumed that minima of negative rotation may be represented, in general character, by the mirror image of the case considered.

Although several cases of minima and possible minima (temperature–rotation curves convex towards the axis of zero rotation) are known, little definite information is available regarding the movement of such minima, and no conclusion can be reached, at this stage, as to whether there are two or four cases of convexity (minima and maxima). If there are only two, representing enantiomorphic relationship, the minima mentioned above, then the rotation region of occurrence indicates the configuration; further, the movement, provided movement of minima occurs, indicates the position of the minima, *viz.*, to the right or the left of the anomalous region on the temperature–rotation diagram.*

If it were shown that a compound of d-*configuration* in its temperature–rotation curves exhibited what *appeared*, on a cursory

* With respect to the position of the minima of positive rotation and the anomalous region, compare Patterson (*loc. cit.*).

glance, to be minima of negative rotation (curves convex to the axis in the *negative* region) though *actually* maxima, then it would be necessary to differentiate this phenomenon * from minima of negative rotation before a criterion, based on minima and maxima (curves convex to the axis), could be established for determining configuration.

The temperature–rotation curves for ethyl thionyl-*d*-tartrate lie in the negative region and are of small curvature, slightly convex *to the axis of zero rotation. The investigation of this compound at* higher temperatures than those recorded yielded no information as to the possibility of a second type of convexity ascending to a *maximum* in the negative region.

d-Ethyl-*n*-decylcarbinol may be cited as a case of a compound showing minima of positive rotation; and *l*-ethyl-*n*-nonylcarbinol and *l*-ethyl-*n*-dodecylcarbinol (Pickard and Kenyon, J., 1913, **103**, 1934) as showing minima of negative rotation. The presence of these minima in the positive and negative regions, respectively, does not prove the configurations of the alcohols conclusively.

Intersection of Temperature–Rotation Curves.

Intersection takes place in a definite order, and indicates under *certain conditions the precise region of a maximum in the dispersion* curve for a particular temperature; it always indicates anomaly.

The following points are summarised from the consideration of the temperature–rotation curves of ethyl *d*-tartrate and its mono- and di-acetyl and monobenzoyl derivatives, also of methyl *d*-tartrate and its mono-acetyl and -benzoyl derivatives :

(1) When intersection occurs, the temperature–rotation curve for a definite wave-length intersects (with increasing temperature)

* Also there would be established four cases, and since each case may involve two types, according to the position of the region of anomaly, the problem would assume a more complex character, and it would be necessary to differentiate minima of positive rotation (*d*-enantiomorph) from maxima of positive rotation (*l*-enantiomorph); in both cases the curves would be convex to the zero axis and situated in the positive region. Similarly for the negative region, the other two cases of minima and maxima would have to be considered.

Expressed briefly, for a compound of *d*-configuration there may exist :

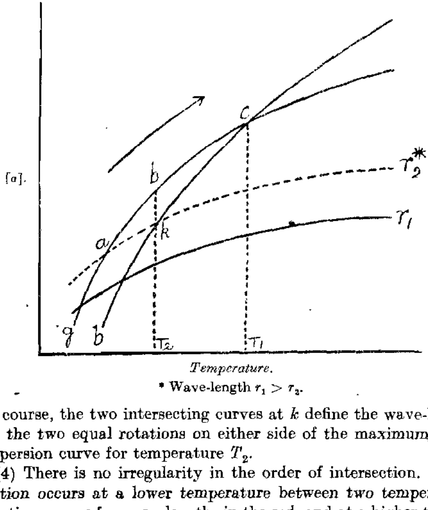
	Type of curves to the zero axis.	Region of rotation.	Example.
Minima of positive rotation.	Convex.	Positive.	*iso*Butyl diacetyl-*d*-tartrate.
Maxima of positive rotation.	Concave.	Positive.	Ethyl *d*-tartrate.
Negative minima.	Concave.	Negative.	Ethyl dibenzoyl-*d*-tartrate.
Maxima of negative rotation.	Convex.	Negative.	Not established.

other temperature-rotation curves in the order of decreasing wave-length, as illustrated in Fig. 4.

(2) A primary intersection c, originating from the intersection of two such curves for two wave-lengths not far apart, indicates a maximum in a dispersion curve—the nearer the wave-lengths the more accurately is the maximum in the dispersion curve defined for T_1.

(3) A secondary intersection k indicates two equal rotations on each side of a maximum b (which is situated on a curve of definite wave-length), provided that b is situated on a small intercept.

FIG. 4.



Temperature.

* Wave-length $r_1 > r_2$.

Of course, the two intersecting curves at k define the wave-lengths for the two equal rotations on either side of the maximum of the dispersion curve for temperature T_2.

(4) There is no irregularity in the order of intersection. Intersection occurs at a lower temperature between two temperature-rotation curves for wave-lengths in the red, and at a higher temperature between two curves for wave-lengths in the blue; thus intersections proceed from the red into the violet with increase of temperature. This is another statement of the well-known fact that maxima in dispersion curves move to decreasing wave-lengths with increase of temperature.

(5) A curve of maximum temperature-rotation may be drawn

lying above the intersections (as a and c) and coinciding with the intercepts (as ac). The curve originates in the red and develops in the direction red → blue as the temperature increases.

(6) Intersection of temperature–rotation curves is a phenomenon which occurs at a lower temperature than intersection (movement of maxima of temperature rotation curves) of dispersion curves in the compounds studied. The two phenomena are intimately associated.

It is assumed that the zero axis and the maxima represent the limits of anomaly, and the presence of maxima without intersection suggests the probability of realising the region of anomaly by suitable choice of solvents, temperature, or derivatives.

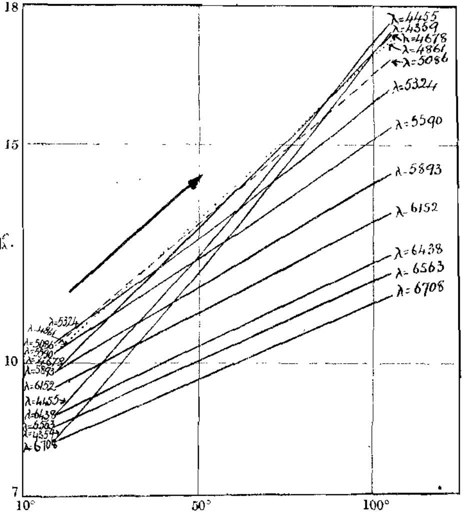
The dispersion diagram is considered as a developing surface on a temperature–wave-length plane, having rotations as ordinates; the surface of access to the negative region of rotation confronts the observer, regions of non-access being more remote. The cross-section is a temperature–rotation diagram and shows part of a surface developing from the red into the violet. Reversal of the movement of the maxima, intersection, etc., in the temperature-rotation curves may take place with change in sign of the rotation temperature coefficient, the zero axis being crossed to the right of the maxima. The temperature–rotation diagram would then represent the cross-section of a surface developing from the blue into the red end of the spectrum, *i.e.*, the position of observation is reversed. The zero rotation–wave-length axis is perpendicular to the plane of Fig. 4, and on the left of the diagram. Consideration of this point reduces the two possible movements of the maxima to one movement; in fact, consideration of the three axes reduce the eight possible cases of maxima and minima (curves concave towards the temperature rotation zero axis) to four.

Intersection of the Temperature Rotation Curves of the Acetyl Derivatives of Ethyl Tartrate.

Figs. 5*a* and 5*b* exhibit a remarkable similarity. The important points to note are: (1) Temperature–rotation curves for λ 4359 intersect temperature–rotation curves for λ 6708, λ 6563, λ 6364, etc., with increase of temperature, without irregularity in the order of intersection. (2) The temperature–rotation curve for λ 4359 (monoacetyl derivative) intersects other temperature–rotation curves in order of decreasing wave-length, and finally becomes part of a curve or envelope of maximum temperature rotation, *above* the highest temperature investigated. Similar comments apply to the curve λ 4678 (diacetyl derivative); this curve becomes part of a curve or envelope of maximum rotation *below* the highest

temperature investigated. (3) The arrow in both diagrams indicates the direction of formation of the envelope of maximum temperature rotation, developing from the yellow-green into the violet. (4) In these derivatives of ethyl *d*-tartrate, intersection of the temperature–rotation curves takes place before the appearance of maxima. (5) The crossing of the axis (diacetyl derivative) is positive. The zero rotation–wave-length axis perpendicular to the plane of the

Fig. 5*a*.

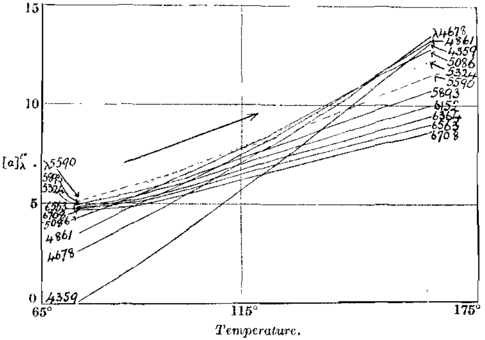


*Rotation–temperature curves for ethyl monoacetyl-*d*-tartrate.*

diagram is to the left. (6) Both diagrams show temperature–rotation curves passing over the maximum of a surface—the nearer part of the surface being formed by temperature–rotation curves of longer wave-length (λ 6708, 6563, etc.), and the remoter part by curves of shorter wave-length (λ 4359, 4678, etc.). Considering the temperature–rotation curve for λ 4861—this curve for lower temperatures lies on a more remote part of a surface; on increase of temperature the curve passes over a maximum on to a nearer

part of the surface, so the passage of the curve over the maximum *is observed from a position in the red end of the spectrum.* (7) The effect of acetylating a single hydroxyl group of ethyl tartrate is to increase the rotation, to remove maxima to higher temperatures, and to remove crossings of the axis to lower temperatures. The effect of acetylating the hydroxyl group of the monoacetyl derivative is to decrease the rotation and to bring the crossings of the axis to a higher temperature. The temperature–rotation diagram (for 17·5° to 95°) for the monoacetyl derivative corresponds, in general character, to the diagram for the diacetyl derivative to the right of 122° (122° to 163°), *i.e.*, the diagram for the monoacetyl derivative has been removed as a whole to a higher temperature.

FIG. 5*b*.



Rotation–temperature curves for ethyl diacetyltartrate.

Maximum Temperature Rotation and the Movement of Maxima in Dispersion Curves.

Temp.	Ethyl mono-acetyltartrate. Max. rot., [α].	λ.	Temp.	Ethyl di-acetyltartrate. Max. rot., [α].	λ.
17·5°	+10·46°	5300	74·1°	+5·13°	5890
25·1	11·06	5170	87·5	5·83	5660
29·5	11·44	5100	101·3	6·68	5480
44·5	12·68	4950	122·2	8·44	5190
59·6	14·11	4830	142·8	10·62	4930
76·8	15·76	4700	162·8	13·39	4665
94·5	17·78	4540			

The above results, obtained by examination of the dispersion curves, show the variation of maximum rotation with temperature,

and the wave-lengths at which maxima occur (dispersion diagram). In Fig. 5 the *envelope of maximum rotation is derived from intersecting* temperature–rotation curves for wave-lengths lying between λ 5300 and λ 4540 (approx.) (monoacetyl derivative) and for wave-lengths lying between λ 5890 and λ 4665 (approx.) (diacetyl derivative) and these wave-lengths indicate the movement of maxima in dispersion curves across the spectrum. An interesting observation for these two closely related compounds is the fact that over the same range of wave-length (λ 5300 to λ 4665) the increase of maximum rotation (5·75°) is, within experimental error, the same for both derivatives, the temperature range in the case of the monoacetyl derivative being 67° (84·2—17·5°), whilst that of the diacetyl compound is 49° (162·8—113·5°). It is difficult, however, to decide from the measurements and graphs the wave-length of maximum rotation for a particular temperature, and this is especially the case with methyl and ethyl tartrates, data for which are given below.

	Methyl tartrate.			Ethyl tartrate.	
Temp.	Max. rot., [α].	λ.	Temp.	Max. rot., [α].	λ.
17·7°	+2·36°	6590	0·8°	+ 5·31°	6150
34·9	3·49	6330	14·4	7·19	5700
59·8	4·75	6090	20·0	7·91	5590
81·2	5·68	5910	40·0	10·41	5310
95·3	6·21	5790	60·0	12·55	5090
100·8	6·43	5750	80·0	14·72	4860
124·9	7·22	5590	100·0	16·31	4710
144·8	7·75	5500	120·0	17·81	4590
162·1	8·15	5440	140·0	18·87	4490

The curvature of the [α]–T curves is concave, and of the [α]–λ curves convex towards the axis. Over the same range of wave-length, λ 6150—5440, the increase of maximum rotation in the case of methyl tartrate is 3·7°, and in the case of the ethyl ester 3·8°; in the former case the temperature range is approximately 109°, and in the latter 29·4°, which indicates the sensitiveness of the ethyl derivative to temperature change.

Summary.

1. The manner of intersection of dispersion curves is discussed.

2. An envelope of maximum dispersion develops in certain tartrates and lactates, with increase of temperature, in the direction red → blue, which indicates movement of maxima in temperature–rotation curves.

3. Movement of maxima of positive rotation (temperature–rotation diagram) is in one direction only, provided the crossing of the axis, $d\alpha/dT$, is positive. A definite movement is of value in deciding configuration. It is necessary to know, in absence of

anomaly, the direction of crossing the axis and the possibility of *intersection of the temperature–rotation curves in the positive* region. Two methods throw light on these points—effect of solvents, and extrapolation by means of a characteristic diagram.

4. Presence and movement of negative minima is assumed to be a temperature relationship for enantiomorphs, and is of rarer occurrence than maxima of negative rotation. Utilisation for configuration purposes depends upon a consideration of the following points: (*a*) Movement of minima; (*b*) the sign of $d\alpha/dT$ on crossing the axis; (*c*) no intersection of temperature–rotation curves in the negative region; (*d*) effect of solvents.

5. The possibility of eight types of maxima and minima having temperature–rotation curves convex towards the axis is considered.

6. Intersection of temperature–rotation curves takes place in a definite order and gives rise to an enveloping curve of maximum temperature rotation.

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EDGBASTON. [*Received, July 26th*, 1927.]

CCXXI.—*A Study of the Anomalous Rotatory Dispersion of Configuratively Related Compounds.*

By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS.

IT has been indicated (this vol., p. 1671) that when anomalous rotatory dispersion is exhibited by *d*-tartaric acid and its derivatives, the anomaly always occurs in the positive region of rotation and crossing of the axis takes place in one way only ($d\alpha/d\lambda$ being positive). A survey of the literature indicates that, when anomaly is realisable for a compound of *d*-configuration, it is confined to the positive region of rotation, and for a compound of *l*-configuration to the negative region; the significance of anomaly, in this respect, has not hitherto been realised. The rule is that anomaly, when realisable, is an absolute guide to relative configuration.

Clough (J., 1918, **113**, 526) has studied the effect of certain halide salts on the optical rotatory powers of *l*-lactic acid, methyl *l*-lactate, *d*-glyceric acid, *l*-malic acid, methyl *l*-malate, *d*-tartaric acid, and methyl *d*-tartrate; he also considered the influence of substituents on the rotatory power of these four acids. Clough assumes that " the optical rotatory powers of similarly constituted compounds possessing the same configuration are in general influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radical attached to the asymmetric carbon atom."

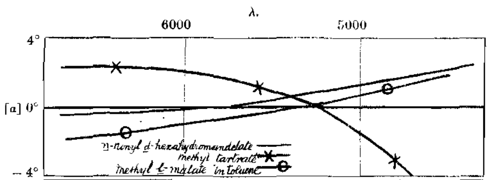
Application of the Criteria of Anomaly to Organic Acids.

Three of the acids, *l*-lactic, *l*-malic, and *d*-tartaric, or their simple esters, exhibit anomalous rotatory dispersion.

Methyl l-*lactate in aqueous solution.* The anomaly becomes more pronounced on dilution, it is confined to the positive region of rotation, and crossing of the axis occurs in one way only.

p.	$[\alpha]^{20°}_{D}$.	$[\alpha]^{20°}_{gr.}$.	$[\alpha]^{20°}_{vi}$.
20	+1·8°	+1·8°	−0·2°
10	+1·3	+1·4	−0·5 (Clough, *loc. cit.*)
5·36	+1·3	+1·4	−0·9

Fig. 1.



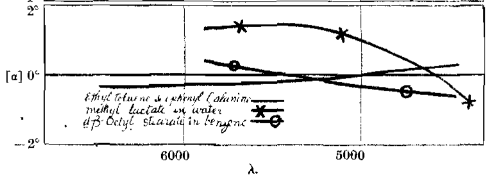


Fig. 2.

The anomaly of this ester for 5·36% concentration is shown in Figure 2.

Methyl l-*malate.* The anomaly is well defined in benzene, toluene, *m*-xylene, *p*-xylene, mesitylene, etc., solution at different concentrations (Grossmann and Landau, *Z. physikal. Chem.*, 1910, **75**, 144).

Conc.	Solvent.		r.	y.	gr.	l.bl.	dk.bl.
2·5	Benzene	$[\alpha]_\lambda$	−0·79°	−0·40°	0·00°	0·40°	0·79°
2·5	Toluene	$[\alpha]_\lambda$	−1·17	−0·39	0·00	1·17	1·95
2·5	*m*-Xylene	$[\alpha]_\lambda$	−1·69	−2·11	−1·69	−1·27	−0·84

Even a 5% solution of methyl *l*-malate in gylcerol shows the anomaly occurring in the negative region (Grossmann, *Trans. Faraday Soc.*,

1914, **10**, 18). The rotatory dispersion of a 5% solution of the ester in toluene is given in Fig. 1.

	r.	y.	gr.	l.bl.	dk.bl.	vi.
$[\alpha]_\lambda$	−1·76°	−0·78°	0·00°	+0·78°	+1·37°	+1·95°

Winther (*Z. physikal. Chem.*, 1902, **41**, 161) also showed that malic *acid in aqueous solution was anomalous in the negative region.*

Methyl d-*tartrate*. In the homogeneous condition at the ordinary temperature (Lowry and Abram, J., 1915, **107**, 1187) and at high temperatures (Wood and Nicholas, *loc. cit.*), in solution (Lowry and Abram, *loc. cit.*), and in the form of derivatives in the homogeneous condition (Wood and Nicholas, *loc. cit.*), the ester retains its characteristic anomaly. The dispersion curve plotted from the data below is given in Fig. 1.

λ	6708	6563	6152	5893	5324	5086	4678	4359
$[\alpha]_\lambda^{17·7°}$	+2·32°	+2·36°	+2·19°	+1·87°	+0·34°	−0·85°	−4·10°	−9·17°

Whenever anomaly is exhibited by *d*-tartaric acid and its derivatives either in the homogeneous condition or in solution, the *anomaly occurs in the positive region of rotation* (for data on the tartrates, see Patterson, J., 1916, **109**, 2, 1139, etc.; Lowry and Austin, *Phil. Trans.*, 1921—22, *A*, **221**, 249).

Anomaly occurs for methyl *l*-lactate in the positive region, for methyl *l*-malate in the negative region, and for methyl *d*-tartrate in the positive region of rotation. Hence *l*-lactic acid is configuratively related to *d*-malic and *d*-tartaric acids and belongs to the "*d*"-series of α-hydroxy-acids. There are no available dispersion data for application of the rule to glyceric acid and its esters (Frankland and McGregor, J., 1893, **63**, 512).

In a later paper, Clough (J., 1925, **127**, 2808) discusses the relative configuration of hexahydromandelic acid: he assigns, on considerations of a similar nature to those given in his earlier paper, the *l-acid to the "d"-series.*

The following data (Wood and Comley, J., 1924, **125**, 2631) show the anomaly of two normal esters :

		λ 6708	5893	5461	4359
n-Octyl *l*-hexahydromandelate ...	$[\alpha]_\lambda^{199·3°}$	+0·99°	+0·53°	−0·15°	−2·35°
n-Nonyl *d*-hexahydromandelate ...	$[\alpha]_\lambda^{201·8°}$	−0·43°	+0·02°	+0·42°	+2·42°

Since the anomaly of *n*-octyl *l*-hexahydromandelate is in the positive region, the acid belongs to the "*d*"-series, whereas the anomaly of the *n*-nonyl *d*-hexahydromandelate assigns this acid to the "*l*"-series. The anomaly was realised in both cases at a high temperature. In Fig. 1, the anomaly of the *n*-nonyl ester is indicated,

This independent proof of the relative configuration of the enantiomorphs of *hexahydromandelic acid is important.*

Comparison of the rotatory power of the amides and esters of *l*-mandelic acid and *l*-hexahydromandelic acid has enabled both Clough (*loc. cit.*) and Freudenberg (*Ber.*, 1923, **56**, 193), by reference to the relative configuration of *l*-hexahydromandelic acid, to assign *l*-mandelic acid to the " *d* "-series, and to show that Hudson's rule, *viz.*, that all hydroxy-acids which yield dextrorotatory amides and hydrazides belong to the " *d* "-series (*J. Amer. Chem. Soc.*, 1918, **40**, 813), requires modification. No derivatives of mandelic acid exhibiting anomaly have been studied, so far, by the authors.

Freudenberg (Freudenberg and Rhino, *Ber.*, 1924, **57**, 2, 1547, etc.), on similar lines to Clough, bases his method for the determination of relative configuration on the assumption that analogous compounds of like configuration undergo corresponding changes of rotatory power under similar conditions. The important feature of his method is the avoidance of factors (solvents, compounds with free hydroxyl, carboxyl, or amino-groups, etc.) which induce anomaly. Where the use of solvents cannot be avoided, extrapolation methods have to be resorted to in order to eliminate solvent effect. A modification of the use of the one-term Drude equation is employed, whereby that part of the dispersion curve is chosen for comparison which differs least from simplicity. Thus comparison of different derivatives with one another is based on the values of K_M deduced from the equation $[M]_n = K_M/(\lambda_n^2 - \lambda_0^2)$ (Rupe and Ackermann, *Annalen*, 1919, **420**, 1).

This method, which attempts to eliminate conditions of anomaly and complexity, is in striking contrast with the rule stated, which requires only the dispersion curves showing visible anomaly. An instance of anomaly from which the configuration could be inferred immediately is ethyl toluenesulphonyl-*l*-alanine, which is anomalous in the negative region (see Fig. 2) (Freudenberg, *loc. cit.*).

Solvent.	Conc.	$\lambda =$	6490	5780	5460	4440
Acetylene tetrachloride	19·62	$\alpha_\lambda^{19°}$ (0·5 dcm.)	−0·33°	−0·27°	−0·17°	+0·29°

Another example, methyl benzoyl-*l*-alanine, taken from the work of Freudenberg is of importance, for it illustrates anomaly by a maximum in the negative region, but crossing of the axis does not occur :

Solvent.	Conc.	$\lambda =$	6490	5780	5460
Pyridine	48·5	$\alpha_\lambda^{20°}$ (0·5 dcm.)	−0·23°	−0·33°	−0·30°

As an additional example, Hewitt (*Biochem. J.*, 1927, **21**, 1, 216)

has shown that tyrosine in 20% hydrochloric acid is anomalous in the negative region :

λ =	6660	5780	5461	4359
$[\alpha]_\lambda^{20°}$	$-7\cdot2°$	$-9\cdot3°$	$-9\cdot6°$	$-7\cdot8°$

In the case of ethyl monobenzoyltartrate (Wood and Nicholas, *loc. cit.*), anomaly of this type occurs at low temperatures, but at higher temperatures a point of inflexion only is realised in the dispersion curve. From the varied examples quoted, it is clear that a maximum, a crossing of the axis, and a point of inflexion, which are indicative of anomaly (compare Lowry, J., 1915, **107**, 1195), together or separately, are sufficient criteria for determining the relative configuration of an asymmetric compound. The theoretical considerations which led to these conclusions are given in another paper.

Karrer and Kaase (*Helv. Chim. Acta*, 1919, **2**, 436), in studying certain reactions in the glutaric acid series with special reference to the measurement of the rotatory dispersion of the products obtained, suggest that the symbols *d*- and *l*- should be given to those compounds which tend to give positive and negative maxima respectively. This tendency refers to rotational values for short wave-length in the positive or negative region; *l*-malic acid is regarded as a d-*acid*, for its dispersion curve (compare Fig. 1, methyl *l*-malate) attains a positive rotational value or tends to a "positive maximum" in the blue region. This conclusion is erroneous. The rotations of *l*-aspartic acid and its ethyl ester tend to a "positive maximum" and the above authors suggest that the acid should be called a "*d*"-acid, which is opposed to the expressed views of Clough that the naturally occurring α-amino-acids, *e.g.*, *l*-aspartic acid, *l*-tyrosine, possess the configuration denoted by "*l*."

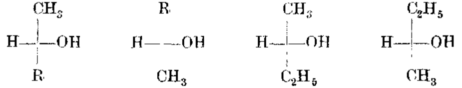
	λ =	6563	5493	5463	4990	4861
l-Aspartic acid ...	$[\alpha]_\lambda$	$-3\cdot54°$	$-2\cdot48°$	$-2\cdot13°$	$-1\cdot18°$	—
Ethyl *l*-aspartate...	$[\alpha]_\lambda$	$+0\cdot98$	$+1\cdot73$	$+2\cdot25$	—	$+3\cdot38$

(Karrer and Kaase, *loc. cit.*)

From the rotations given, anomaly is seen to occur in the negative region, and it is assumed that *l*-aspartic acid is configuratively related to *l*-tartaric acid. The "maxima" referred to above are, of course, not real maxima exhibited by anomalous dispersion curves, but simply denote ascent of the dispersion curves for short wave-lengths in (or to) the positive or the negative region. Since *d*-α-hydroxyglutaric acid, ethyl *d*-pyroglutamate, and *d*-butyrolactone-γ carboxylic acid (compare Karrer and Kaase, *loc. cit.*, for designation "*d*".) all exhibit anomaly in the negative region, they should be considered to be configuratively related to *l*-tartaric acid.

Configuratively Related Alcohols.

The application of the rule to optically active alcohols is of interest. The authors regard the "*d*"- and "*l*"-methyl- and "*d*"- and "*l*"-ethyl-carbinols as two distinct series, quite as distinct as are the series of esters derived from "*d*"- and "*l*"-lactic [CH_3·CH(OH)·CO_2H] and from "*d*"- and "*l*"- α-hydroxybutyric [CH_3·CH_2·CH(OH)·CO_2H] acids. For reasons discussed later the "*d*"- and "*l*"- methyl series are represented by the space formulæ (I) and (II).



"*d*-Methyl" series. (I.)	"*l*-Methyl" series. (II.)	"*d*"-Methyl-ethylcarbinol. (III.)	"*l*"-Methyl-ethylcarbinol. (IV.)

The first member, dimethylcarbinol, is inactive. The second members are (III) and (IV). The members of the "*d*-methyl" series are all dextrorotatory (Pickard and Kenyon, J., 1911, **99**, 49) and therefore the members of the enantiomorphic series, *viz.*, the "*l*-methyl" series, are all lævorotatory.

The experimental grounds (effect of temperature is considered in another section) for this view are :

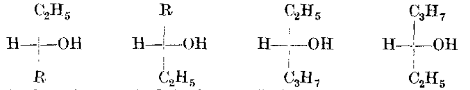
(1) "*d*"-Methylethylcarbinol has been proved to have the above space formula from its relationship to *d*-butane-αγ-diol, which is configuratively related to *d*-lactic acid (Levene, Walti, and Haller, *J. Biol. Chem.*. 1927, **71**, 465) belonging to the "*l*"-series of α-hydroxy-acids, and also to *l*-α-hydroxybutyric acid (Levene and Haller, *ibid.*, **74**, 343) belonging to the "*d*"-series of α-hydroxy-acids. This paradox will be discussed later. In the methyl series the alkyl radicals differ only in the length of the normal chains. The bottom radical for the "*d*"-series being the longer, for *d*-methylethylcarbinol has been proved experimentally to be configuratively related to "*d*"-α-hydroxybutyric acid, the replacement of the carboxyl group (top group) by the methyl radical causes no change in configuration.

(2) Certain esters of the higher *d*-alcohols exhibit visible anomaly in the positive region. Data for three typical esters are :

Ester.	Solvent.	$[\alpha]_D$.	$[\alpha]_{gr.}$.	$[\alpha]_{vt.}$.
d-β-Octyl *n*-nonoate	Benzene	+0·28°	±0°	−1·89°
d-β-Octyl stearate	Benzene	+0·32°	±0°	−0·63°
		(Pickard and Kenyon, J., 1914, **105**, 830.)		
d-β-Octyl succinate	Ethyl alcohol	$[\alpha]_{5893}^{18°} = +1·77°$	$[\alpha]_{5461}^{18°} = +1·67°$	
		$[\alpha]_{4358}^{18°} = -0·29°$		
		(Hall, J., 1923, **123**, 43.)		

Further instances of the anomaly of these esters are: β-octyl, β-nonyl, β-decyl, β-undecyl, and β-tridecyl acetates, also β-undecyl propionate (Pickard and Kenyon, *loc. cit.*). The dispersion curve for *d*-β-octyl stearate is given in Fig. 2.

Similarly the ethyl series is formulated as in (V) and (VI). R can

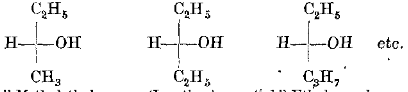


"*d*-Ethyl" series. (V.) — "*l*-Ethyl" series. (VI.) — "*d*"-Ethylpropylcarbinol. (VII.) — "*l*"-Ethylpropylcarbinol. (VIII.)

be equal to or greater than, but never less than, C_2H_5, for if it were less the alcohol would belong to the methyl series. The first member, diethylcarbinol, is inactive; the second members are (VII) and (VIII). The members of the "*d*-ethyl" series are all dextrorotatory (Pickard and Kenyon, J., 1913, **103**, 1923) and therefore the members of the enantiomorphic series, *viz.*, the "*l*-ethyl" series, are all lævorotatory.

The grounds for the above formulation are:

(1) *l*-Methylethylcarbinol is a member of the "*l*"-methyl series; *d*-ethylpropylcarbinol is a member of the "*d*"-ethyl series, and the relationship is as follows:



"*l*"-Methylethylcarbinol. — (Inactive.) — "*d*"-Ethylpropylcarbinol.

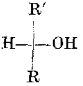
Rotation: *Negative.* — *Zero.* — *Positive.*

This passage from the *l*-methylethylcarbinol (configuration "*l*") by increasing the bottom group through inactive diethylcarbinol to the dextrorotatory ethyl series involves a change of configuration, for the dextrorotatory members of the ethyl series are of "*d*"-configuration from the consideration of region of anomaly, temperature–rotation curves, molecular rotation, etc. Thus on experimental grounds in the "*d*"-alkyl series R is greater than R′; when R is equal to R′ asymmetry disappears, and when R is less than R′ the "*l*"-enantiomorphs of the R series are obtained [see (IX)].

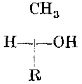
From the graphical (space model) conception the distinction between a "*d*"- and "*l*"-configuration depends on the relative length of the normal chains represented by R and R′, two assumptions being possible for a "*d*"-configuration, namely R<R′ and R>R′.

If R is originally less than R′, then on increase of R the alcohol passes through zero rotation to an "*l*"-configuration which is not in accordance with the "*d*"-configuration assigned to these alcohols on general grounds.

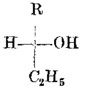
(2) Two instances of anomaly with regard to the "*d*"-ethyl series (Kenyon, J., 1914, **105**, 2246, 2254) could be inferred from the tabulated data, but the facts that no mention of anomaly is given in the text and that these two cases do not appear to be in harmony with the rest of the data, point to their being typographical errors. From characteristic diagrams for certain of the esters, however, the region of anomaly is inferred to be in the positive region (compare diagram,



(IX.)



"*d*-Methyl" series.
(X.)



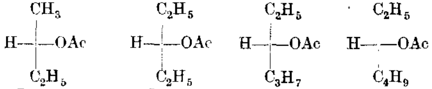
"*d*-Ethyl" series.
(XI.)

Kenyon, *loc. cit.*, p. 2234); further, the temperature–rotation curves for certain of the *d*- and *l*-alcohols exhibit maxima and minima of positive and maxima and minima of negative rotation, respectively, the presence of which is confirmatory though not conclusive evidence for the configurations.

(3) The rotation data are in accord with this classification. The first optically active member, ethylpropylcarbinol, has a rotation $[\alpha]_D^{20°} = +1{\cdot}97°$, and as the series is ascended the molecular rotation *increases* in a normal manner. Kenyon (J., 1914, **105**, 2226) formulated the series as in (X) and (XI) and regarded dextrorotatory methylethylcarbinol as the first member of each series. According to his classification, this carbinol is the first member of the ethyl series (on our classification it is the first optically active member of the methyl series) and has rotation value $[\alpha]_D^{20°} = +13{\cdot}87°$, which is not in accordance with the rotational values of the "*d*-ethyl" series, the molecular rotation of which increases from zero rotation. Kenyon's view also leads to difficulties in considering the acetates of the "ethyl" series of carbinols. Kenyon (*loc. cit.*, p. 2231, Fig. 2) finds that the acetate of γ-butanol (dextrorotatory methylethylcarbinol) has a positive rotation. The acetate of diethylcarbinol is, of course, inactive, whereas the acetate of ethylpropylcarbinol is dextrorotatory. All the higher acetates of the series are of negative rotation, so there is an *unexplained* second zero between the acetates of γ-hexanol and γ-heptanol.

On the view put forward, no such irregularities occur, for (1) the acetate of methylethylcarbinol belongs to the methyl series, (2) the

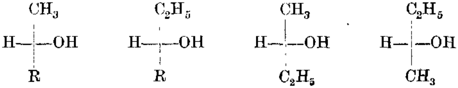
first zero denotes the discontinuous transition from the "methyl" to the "ethyl" series, (3) the acetate of ethylpropylcarbinol is the first member of the "ethyl" series, and (4) the second zero relates to the ethyl series only, the acetate of the first optically active member, ethylpropylcarbinol, being positive, and as the alkyl chain increases so the acetates pass normally from the positive to the negative region of rotation.



Rotation:	Positive.	Zero.	Positive.	Negative.
Configuration:	"*d*"		"*d*"	"*d*"

"*d*"-ethyl series.

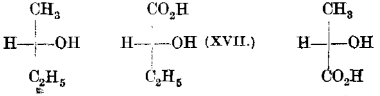
Clough (P., 1913, **29**, 357) represents the "*d*"-methyl and "*d*"-ethyl series as in (XII) and (XIII) and considers that similarity



(XII.) (XIII.) (XIV.) (XV.)

in the sign of rotation accompanies similarity of configuration so long as $R > CH_3$ and $R > C_2H_5$ for the two series respectively. When he considers the first optically active member of each series, *viz.*, (XIV) and (XV), he arrives at the "paradox that the simplest *members of the two configuratively similar series are enantiomorphic* forms of the same substance." The issue has been confused by allowing R to have values not only equal to and greater than, but also less than, C_2H_5, *viz.*, CH_3, and so erroneously *l*-methylethylcarbinol is made a member of the ethyl series.

The restricted definition of configuration as applied to the α-hydroxy-acids no longer serves when the alcohols are considered; methylethylcarbinol is a compound of relative configuration "*d*" on comparison with "*d*"-hydroxybutyric acid, but of relative configuration "*l*" on comparison with "*l*"-lactic acid.

(XVI.)  (XVII.) (XVIII.)

The configuration of a compound is regarded as "*d*" or "*l*" when the electron frequencies of the four pairs of coupling electrons are

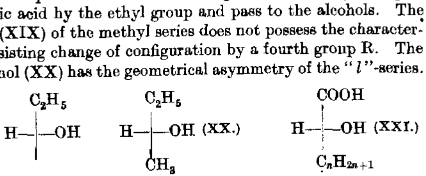
in the order of magnitude corresponding to a "*d*"- or "*l*"-α-hydroxy-acid, the sign of the high-frequency term in the Drude equation being taken as a criterion of the order. In (XVII) and (XVIII) the frequencies will be in the reverse order. On the assumption that the frequencies corresponding to the linkages decrease in the order $C-H > C-OH > C-CO_2H > C-CH_3 > C-C_2H_5$, (XVI) will have the same order as (XVII) but the reverse of (XVIII); accordingly the configuration of (XVI) is "*d*." Certain derivatives of higher members of the series (XVI) show anomaly in the positive region, *i.e.*, the high-frequency term is positive.

Configuration as at present defined has no meaning outside the series of related compounds to which it is applied. The above extension applies to all series, and accordingly all series are designated as "*d*"- or "*l*"-series. This designation not only implies the same order of frequencies but also a corresponding similarity of shape (compare Thomson, *Phil. Mag.* 1920, **40**, 713), *i.e.*, the geometrical distribution of the groups in space.*

In the *α-hydroxy-acids, two methods of determining relative* configuration have been employed: (1) Proof of the correspondence of the three groups by processes of synthesis and degradation; (2) deductions from factors influencing optical rotatory powers. Only in those cases where the former has been adopted and in which no Walden change has been involved can the space formula be regarded as absolutely proved. The latter method is open to criticism, yet space formulæ are in all probability assigned correctly, for the electron frequencies of the linkages C–H, C–OH, $C-CO_2H$ are very likely far removed from the normal, and so the order of the frequencies is not altered by substitution of a group R (higher alkyl, $CH_2{\cdot}CO_2H$, *cyclo*hexyl, phenyl, etc.) for CH_3 in lactic acid. Stated in another way, the fourth group R modifies but does not change the shape typical of "*d*"- or "*l*"-compounds.

The case is quite different when we replace the carboxyl group in "*d*"-lactic acid by the ethyl group and pass to the alcohols. The grouping (XIX) of the methyl series does not possess the characteristic of resisting change of configuration by a fourth group R. The "*l*"-alcohol (XX) has the geometrical asymmetry of the "*l*"-series.

(XIX.) (XX.) (XXI.)



* Neither the electrons nor the atomic groups are regarded as situated at the corners of a regular tetrahedron (compare Lindman, *Ann. Physik*, 1924, **74**, 6, 541, etc.).

On replacement of the methyl group first by C_2H_5 and then by C_3H_7, the alcohol passes through the regular tetrahedron to the geometrical asymmetry of the " *d* "-series.

Zero rotation for all wave-lengths due to passage of the shape through the regular tetrahedron to the enantiomorph is quite distinct from zero rotation for one particular wave-length; for *passage through anomaly involves modification but not change in* the typical shape. Although anomaly indicates when compounds have a similarity of geometrical asymmetry, yet the assignment of space formulæ, even when compounds with the linkages C–H and C–OH in common are being considered, requires a knowledge of the order of the frequencies of the four groups involved (that is, the order of the deflexion of the groups), *i.e.*, a knowledge as to which of the groupings in the derived compound deflect similarly to those in the *original compound.*

The synthetical work of Levene and Haller (*loc. cit.*) has been taken as the decisive factor in assigning space formulæ to the " *d* "-methyl and " *d* "-ethyl series of carbinols which may be considered as derived from the acids (XXI)—the " *d* "-methyl series by replacement of carboxyl by methyl, provided $C_nH_{2n+1} > CH_3$; *similarly*, the " *d* "-ethyl series, provided $C_nH_{2n+1} > C_2H_5$.

Influence of Radicals and Temperature.

Consider " *d* "-lactic and " *d* "-α-hydroxybutyric acids, the esters of which form two distinct homologous series which are structurally related. If we select a corresponding ester, *viz.*, the R ester from each series, these two esters are also members of an homologous series of " *d* "-α-hydroxy-esters, the first two members being $CH_3 \cdot CH(OH) \cdot CO_2R$ and $C_2H_5 \cdot CH(OH) \cdot CO_2R$.

Removal from the region of possible anomaly proceeds by increase of the *n*-alkyl chain of the ester grouping in the esters of " *d* "-lactic acid, this removal being indicated by the approach to and formation of maxima in the temperature–rotation curves of the esters.*

Increase of the alkyl group attached to the asymmetric carbon

* A point of further importance is that the maximum rotation for a definite wave-length is at a lower temperature for the octyl than for the butyl ester. A more recent determination of the maxima for *n*-octyl *l*-lactate has been made with the following results (compare Wood, Such, and Scarf, J., 1923, **123**, 600):

Maxima occur at	103—105°	for	λ 6708
	108°	,,	6563
	113—115°	,,	6438

atom decreases the rotation and brings a particular ester nearer to the anomalous region :

Ethyl hydroxybutyrate	$[\alpha]_D^{15}$	$+1{\cdot}9°$	(Guye and Jordan, *loc. cit.*)
,, *l*- ,,	$[\alpha]_D^{22}$	$-3{\cdot}83°$	(Levene and Haller, *J. Biol. Chem.*, 1927, **74**, 343.)
,, lactate	$[\alpha]_D^{15}$	$+8{\cdot}64°$	

In the case of the carbinols, a particular alcohol is a member of a series of structurally related alcohols, besides being a member of the "*d*"-methyl, "*d*"-ethyl series, etc. In this series R is the constant group and R′ the changing alkyl group. Increase of R′ ultimately brings the carbinol to the axis :

Methylpropylcarbinol	$[\alpha]_D^{20}$	$+13{\cdot}70°$	(Pickard and Kenyon, *loc. cit.*)
Ethylpropylcarbinol	,,	$+\ 1{\cdot}97°$	

(The third member being inactive, further increase of R′ would give the first optically active member of the "*l*"-propyl series.)

Thus a transition from the positive to the negative region takes place with change of configuration, the middle member, which separates the "*d*"- from the "*l*"-series, being inactive. They form a simple series of optically active compounds restricted with respect to the "*d*"-compounds to the positive region, which is not the case with the hydroxy-acids, where the upper and lower groupings never become identical. Passage into the negative region may be attained by acylation of the hydroxyl group or acylation and subsequent solution, but this depression of the rotation of the asymmetric carbon atom, forced, as it were, to give negative rotations, results generally in an ill-defined anomaly, or the derivative is situated in a particular part of the negative region where anomaly cannot be attained in the visible region either by change of temperature or by solution.

The following points are of interest with respect to the increase of the alkyl group R in the "*d*"-ethyl series, positive numerical values of the molecular rotation being considered (Pickard and Kenyon, J., 1913, **103**, 1934) : (*a*) The rotation increases with increasing temperature for the propyl and butyl members; (*b*) the amyl, hexyl, and heptyl members exhibit maxima in their temperature–rotation curves, the maxima for a particular wave-length moving to a *lower temperature* with increase of the alkyl chain, the octyl member, though showing maxima, being exceptional [compare the movements of maxima with increase of the alkyl grouping in the tartrates, certain of the members being exceptional (Patterson, J., 1913, **103**, 173; 1904, **85**, 765; Frankland and Garner, J., 1919, **115**, 643)]; (*c*) the nonyl, decyl, and undecyl members exhibit minima, the

minima moving to a *higher temperature* and higher rotation with increase of the alkyl chain, the dodecyl member being exceptional [compare the movement of minima for members of the " *d* "-methyl series (Pickard and Kenyon, J., 1912, **101**, 626)]; (*d*) the rotatory powers of the tridecyl and pentadecyl members decrease with temperature as far as they have been investigated. From these considerations it is assumed that increase of R removes the alcohol in a direction away from the approach to the zero axis, certain members being exceptional. Just as minima are displaced to a higher temperature, so maxima are displaced to the lower temperature.

Increase of the R' group has in general the reverse effect. Methylamylcarbinol exhibits minima (temperature–rotation curves), and ethylamylcarbinol maxima, minima being more removed, relatively, from the approach to a zero axis than maxima. The temperature–rotation curves for methylpropylcarbinol decrease with temperature; those for ethylpropylcarbinol increase with temperature, and it is assumed from analogy with the tartrates that the former are situated with reference to the approach to the zero axis, on a more remote, and the latter on the nearer part of a maximum rotation surface. Consideration of the data given by Pickard and Kenyon (J., 1911, **99**, 45; 1913, **103**, 1934; 1912, **101**, 620) shows that increase of R' from the methyl to the ethyl grouping causes the minima to move to a lower temperature:

	Temp. of minimum rotation for $[\alpha]_D$.
Methyl-*n*-nonylcarbinol	178° (about) (calculated by authors).
Ethyl- ,, ...	100—120° (Pickard and Kenyon).
Methyl-*n*-decylcarbinol	169° (about) (calculated by authors).
Ethyl- ,, ...	120—140° (Pickard and Kenyon).
Methyl-*n*-undecylcarbinol	189° (about) (calculated by authors).
Ethyl- ,, ...	140—160° (Pickard and Kenyon).

In the above the temperature–rotation–wave-length surface f each individual member is compared, and the relative displacemer of the surfaces, although discontinuous with each other, a considered.

l-α-Naphthylmethylcarbinol and *d*-α-naphthyl-*n*-hexylcarbinol a anomalous in the negative and positive regions respectively, and a considered to be of "*l*"- and "*d*"-configurations respectively:

	$[M]_D^{Max.}$.	Temp. of maximum.	$[M]_D^{10°}$
*Naphthylmethylcarbinol**	67·50°	140°	21·19
α-Naphthyl-n-hexylcarbinol	106·8°	180°	27·24

(Pickard and Kenyon, J., 1914, **105**, 1115; Kenyon and Pickard, 1914, 2644.)

* Comparable numerical values for $[M]_D$.

Increase of the alkyl chain results in (*a*) an increased rotation at the maximum, (*b*) movement of the maximum for a particular wave-length to a *higher* temperature, and (*c*) passage across the zero axis into the negative region.

The cases of phenyl-methyl- and -ethyl-carbinols are particularly interesting :

	$[M]_D^{Max.}$	Temp. of maximum.	$[M]_D^{20°}$.	$[M]_D^{140°}$.
Phenylmethylcarbinol	—	—	50·94°	46·98°
Phenylethylcarbinol*	48·28°	120°	35·17°	46·74°

(Pickard and Kenyon, *loc. cit.*)

* Comparable molecular numerical values.

Neither of these alcohols shows visible anomaly. Phenylmethylcarbinol does not exhibit maxima in its temperature–rotation curves —its rotation continually decreases with temperature. Since the molecular rotation change from 20° to 40° is 0·3°, and that from 120° to 140° is 0·98°, it is inferred that the alcohol is tending to maximum rotation at low temperature and, in addition, that increase of the methyl to the ethyl group has brought the maximum into the visible region, *viz.*, to a *higher* temperature. Increase of the alkyl group results in (*a*) a decreased rotation at the lower temperature, (*b*) the realisation of a part of a surface of maximum positive rotation (for the compound of " *d* "-configuration). From analogy with the naphthylcarbinols, the region of possible anomaly is to the left (temperature–rotation diagram), and this deduction is supported by (*c*) complexity of character. Phenylmethylcarbinol is simple and phenylethylcarbinol complex below 40° (approx.) (Pickard and Kenyon, *loc. cit.*) (Characteristic diagram—intersection of violet and green lines in positive region.)

It is assumed from these considerations that both the dextrorotatory alcohols are of " *d* "-configuration, and that the movement of the maxima is due to the change in the alkyl group. Absolute proof and unassailable evidence would be given by the higher alcohols of this series.

The data at present available are not sufficient to make a decision with respect to space formulæ.

For simplicity of treatment only four cases of series movements of maxima and minima, two for each, for a particular wave-length have been considered ; the discussion of other possible cases has been deferred. In all the cases here discussed, the anomalous region is towards the left (compare treatment of movement of maxima and minima, this vol., p. 1696).

A survey of the *iso*propyl series (Pickard and Kenyon, J., 1912, **101**, p. 623, diagram) indicates an increase of specific rotation as the methyl increases to the butyl grouping ; thereafter, as the alkyl

group increases, a decrease of rotation is noted, with rather better definition of maxima in temperature–rotation curves. The maxima are considered to be moving to the higher temperature with increase of the alkyl chain; further, the curves appear to be approaching to minima on the right, and the approach to the anomalous region is considered then to be to the left. If these points are conceded, it follows from analogy with other carbinols that these carbinols also are of " *d* "-configuration.

In conclusion, as an application of the fundamental criterion, the configuration, " *d* " and " *l* " respectively, of the following alcohols is inferred from the anomalous dispersion of derivatives.

	$[\alpha]_{D.}$	$[\alpha]_{Ye.}$	$[\alpha]_{Gr.}$	$[\alpha]_{Vi.}$
d-Benzylmethylcarbinyl stearate ... (approx. 5% CS_2 solution)	+0·54°	+0·31°	+0·23°	−1·31°
Sodium *l*-*ac*-tetrahydronaphthyl phthalate (H_2O solution)	−1·24°		−1·02°	+1·10°

(Kenyon and Pickard, *J.*, 1914, **105**, 2262, 2677.)

A Case involving Asymmetric Nitrogen.—Nicotine is lævorotatory and its salts are dextrorotatory. Lowry and Singh (*Compt. rend.*, 1925, **181**, 909) have shown that the alkaloid in the homogeneous condition at 20° exhibits simple rotatory dispersion in the negative region. Gennari (*Z. physikal. Chem.*, 1896, **19**, 130) observed that an equimolecular mixture of nicotine and glacial acetic acid, withir certain limits of dilution with water, exhibits anomaly in the positiv region ($d\alpha/d\lambda$ positive). Nicotine salts are therefore assumed to b of relative configuration " *d*."

The rotation of the base is due to the asymmetry of the α-pyrrol idine carbon atom; in the salts, however, a new centre, the asyn metric pyrrolidine nitrogen atom, is involved (Lowry, *Chem. an Ind.*, 1927, **46**, 102). No decision as to the configuration of the fre base is at present possible, for the respective configurations an dominance of the two centres are unknown.

Patterson and Fulton (J., 1925, **127**, 2435) have shown that tl rational zero (for nicotine and its sulphate) is + 3°, and if th rotation could be realised for the green rays, the rotatory dispersi would be visibly anomalous in the positive region. But a deducti as to the relative configuration of the *free* base from the data giv would require careful consideration of the occurrence and moveme of maxima in the negative region in the temperature–rotation curv for the homogeneous base at high temperature, and similarly for t base in inert solvents, and also the construction of separate charact istic diagrams, as well as a composite one.

The fact that nicotine sulphate and nicotine in various solve

fit on the same characteristic diagram, suggests that the α-pyrrolidine carbon atom is of relative configuration "*d*."

Summary.

(1) Anomalous rotatory dispersion is a trustworthy criterion for determining relative configuration.

(2) The configurations of *l*-lactic, *l*-malic, *d*-hexahydromandelic, and *d*-tartaric acids, as shown by their anomalies, are "*d*," "*l*," "*l*," and "*d*" respectively, which is in agreement with the configurations assigned to these acids by other workers.

(3) The non-empirical nature of this criterion is illustrated by (*a*) *l*-alanine, *l*-tyrosine, and *l*-aspartic acid, which are configuratively related to *l*-tartaric acid, and (*b*) certain series of alcohols.

(4) The distinction between "*d*"- and "*l*"-alcohols containing normal straight chains depends only on their relative lengths, since all other factors are eliminated.

(5) Movement of maxima and minima for a particular wave-length in an homologous series of configuratively related compounds has been discussed.

(6) Series of alcohols have been considered with respect to: (*a*) Configuration; (*b*) rotation change with temperature for each individual member, particularly with regard to the region of approach of temperature–rotation curves to the zero axis and to a zero rotation–temperature–wave-length plane; (*c*) movements of maxima and minima as the series is ascended. A series, none of the members (or derivatives) of which exhibits anomaly, is then considered with respect to (i) temperature–rotation curves and (ii) movements of maxima and minima, as the series is ascended. From analogy, conclusions are drawn as to configuration relationship.

(7) The configuration of nicotine and its salts is considered.

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EDGBASTON.
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CCXXII.—*The Rotatory Dispersion of Optically Active Co-ordination Compounds.*

By CHARLES EDMUND WOOD and SYDNEY DIGGARY NICHOLAS.

THE principle relating to anomalous rotatory dispersion in co-ordination compounds is not only of interest as showing its general applicability bnt is also of importance in a field where opposing views are held regarding configuration relationships. Further, it is the application of "propriétés physiques," to which Pasteur

refers ("Leçons sur la dissymétrie moléculaire," 1860) when he states "dont l'une est l'image de l'autre en ce qui concerne toutes les propriétés physiques qui dépendent de ce groupement stéréométrique."

Pasteur, regarding especially the physical property of crystalline shape, postulated that an asymmetric molecule will produce enantiomorphous crystals. and Jaeger, in the course of his crystallographic investigations of this principle, determined the dispersion of certain complex salts for different concentrations (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **17**, 1217; 1915, **18**, 49; 1917, **20**, 244, 263; 1918, **21**, 203, etc.; *Bull. Soc. chim.*, 1923, **33**, 853; *Rec. trav. chim.*, 1920, **38**, 171).

General Occurrence of Anomaly.—In the case of dextrorotatory * potassium cobaltioxalate, the rotation increases rapidly at first as the wave-length attains a maximum at λ 6000, rapidly decreases, becomes zero at λ 6260, reaches a maximum negative value at λ 6400, and then the curve ascends to the zero axis. The two maxima denote passage through an active absorption band, and although crossing of the axis to the right of the band does not occur, yet the data suggest that crossing, if it had been realised, would have made $d\alpha/d\lambda$ positive.

In the case of dextrorotatory potassium chromioxalate, actual crossing takes place. The curve is similar in type to that described above. A broad absorption band (λ 5200—6000) is present, giving rise to true anomaly; further, crossing of the zero axis from the negative to the positive region of rotation was realised at about λ 6360. This anomaly, as distinct from true anomaly, indicates definitely that the compound is configuratively related to "*d*"-tartaric acid.

An interesting example of a compound of relative configuration denoted by the symbol "*l*" is dextrorotatory potassium rhodioxalate. The dispersion curve investigated lies between wavelengths λ 4860 and 7000, crossing the axis at 5970 from the positive to the negative region of rotation ($d\alpha/d\lambda$ negative), and for this wave-length there is no absorption band.

The dispersion curve for dextrorotatory potassium irido-oxalate has been investigated between λ 4790 and 6800 and lies wholly in the positive region. The dispersion is normal for longer wavelengths, but as the wave-length decreases, inflexion develops, the curve tending to reach a maximum and to become parallel to the zero axis below λ 5100. The parallelism is due to an absorption band. Bruhat (*Bull. Soc. chim.*, 1915, **17**, 226) has investigated this region and finds that the maximum is due to true anomalous

* Actually the dispersion of the lævorotatory salt was investigated.

rotatory dispersion, for it is accompanied by circular dichroïsm; he has measured both the ellipticities and the rotation. There is complete analogy, therefore, in this respect between asymmetric iridium and asymmetric carbon (compare Cotton, *Ann. Chim. Phys.*, 1896, **8**, 347). The portion of the curve between λ 5420 and 6800 is approximately parallel to that for the rhodium compound, the main difference being the proximity of the absorption band in the visible region. The dispersion curve has been displaced as a whole to a greater wave-length. This disposition of the curve suggests that the crossing of the axis is removed into the red end of the spectrum. If this is the case, the relative configuration is "*l*."

This independent decision that the dextrorotatory cobalt and chromium salts are of "*d*" configuration is in accordance with both Werner's and Jaeger's conclusions. The view that the dextrorotatory rhodium and iridium compounds are of "*l*" configuration, though in harmony with Werner's view, is opposed to Jaeger's.

Opposing Views on Relative Configuration.—Werner (*Ber.*, 1912, **45**, 1228; *Bull. Soc. chim.*, 1912, **11**, 1) considered that those asymmetric isomerides having corresponding relative configurations gave the more sparingly soluble salts with the same active acid or base but did not necessarily give rotatory power of the same sign; for instance, the isomerides set free from the sparingly soluble triethylenediamine-chromium and -cobalt salts were dextrorotatory and configuratively related to the corresponding sparingly soluble rhodium salt, which was lævorotatory. Werner founded this law, which involves sign of rotation, relative configuration, and analogous solubility relationships, on the following facts:

(1) Compounds of opposite rotatory power were obtained by chemical reactions which are not accompanied by a change of configuration of the complex grouping (Co en_2)

(2) Both the dextrorotatory chloronitrocobaltic and the lævorotatory chloro*iso*thiocyanatocobaltic series gave salts with *d*-bromocamphorsulphonic acid which were much less soluble than the corresponding salts with the *l*-acid. By the action of potassium thiocyanate on the chloride of the former, and of sodium nitrite on the chloride of the latter, the same dextrorotatory nitro*iso*thiocyanatocobaltic chloride is obtained.

(3) The lævorotatory tetraethylenediamine-μ-aminoperoxodicobaltic series is transformed by the action of nitrous acid into the dextrorotatory tetraethylenediamine-μ-aminonitrodicobaltic series, and both series give difficultly soluble *d*-bromocamphorsulphonates. Such transformations as the above led to no inconsistencies, thus making unlikely a Walden inversion. Further, *d*-cobalt-, *d*-chrom-

ium-, and *l*-rhodium-triethylenediamine salts are configuratively related. Werner considered that the sign of the rotatory power depends on (*a*) the nature of the central atom, and (*b*) the radicals which occupy the other two co-ordination positions.

Jaeger opposes Werner's conclusions on the following grounds. (1) In the analogous optically active complex salts of cobalt and rhodium the two metals will replace each other isomorphously. (2) The less soluble chloride-*d*-tartrates of triethylenediamine-cobalt and -rhodium possess different crystalline forms, the former having a triclinicpedial symmetry and crystallising with 5 mols. of water, whereas the latter has a monoclinic and perhaps sphenoidical symmetry and crystallises with 4 mols. of water. This absence of isomorphism of cobalt and rhodium in analogous combination led to the deduction that they are not of the same but of opposite relative configuration. The triethylenediaminerhodium iodide set free from this chloride-*d*-tartrate, together with all salts derived from it, is lævorotatory, the corresponding cobalt salts being dextrorotatory, so that rotatory power of opposite sign accompanies opposite relative configuration.

Jaeger regards the replacing of the central cobalt by a rhodium atom as manifesting itself only by a difference in magnitude, but not in sign, of the rotation; and he further regards the radicals, basic or acidic, arranged unsymmetrically around the central metallic atom and the specific asymmetry of the arrangement as determining in the first instance the sign of the rotation.

The dispersion curves of the dextrorotatory triethylenediamine salts of cobalt and chromium are analogous and do not resemble those for the corresponding salts of rhodium. The chief point of interest is that the former are normal; the curve for triethylenediaminechromium iodide runs almost parallel to that for the corresponding cobalt salt, but, unlike the latter, it exhibits a point of inflexion. The dispersion curves for triethylenediaminerhodium iodide, bromide, and nitrate are remarkable: for a particular wave-length, increase of rotatory power is in the order given; for longer wave-lengths, the curves are practically parallel; for shorter wave-lengths, the curve for the bromide diverges from that of the nitrate and converges on that of the iodide. They all show inflexion and maxima or approach to maxima; for instance, the dispersion curve for the iodide ascends to a maximum, becomes almost parallel to the zero axis between λ 4420 and 4010, and thereafter from λ 4010 to 3700 (measurements uncertain) the rotatory power decreases.

In the literature there is no mention of the maxima being due to true anomaly. The order of the absorption bands is to a shorter

wave-length in passing from cobalt through chromium * to rhodium.

The published data, which are not conclusive, appear to indicate that (1) both the cobalt and the chromium salts are passing to an active absorption band in the *positive* region, where they will exhibit true anomaly, and (2) the rhodium salts exhibit anomaly in the positive region, the active absorption band being therefore in the *negative* region. Assuming these points and Werner's law, we may draw up the following scheme :

Series.	Sign of rotation.	Relative configuration deduced from dispersion.	Less soluble compound. (General type : "*l*"-complex *d*-acid.)
Co en_3	Dextro	"*l*"	Chloride-*d*-tartrate.
Cr en_3	Dextro	"*l*"	*d*-Camphornitronate.*
Rh en_3	Lævo	"*l*"	Chloride-*d*-tartrate.

* The same optically active acid was not employed in this case as resolving agent. Werner (*loc. cit.*) considers the above series to be configuratively related.

The dispersion diagram would now be a comparative series of curves (those for cobalt and chromium situated in the positive region, that for rhodium in the negative region), passing and, in the case of rhodium, about to pass to an active absorption band in the positive region.

A further important point noted by Jaeger is that the crystals of the optically active triethylenediamine-cobalt and -rhodium nitrates, which in solution have the *opposite* sign of rotation, exhibit sphenoids of the *same* algebraic sign, *viz.*, the dextrorotatory cobalt salt (relative configuration "*l*" by the argument above) exhibits a right-handed sphenoid (+) and the lævorotatory rhodium nitrate ("*l*") also shows the right-handed form.

Confirmatory Evidence of the Complex Oxalates and Malonates.

If it be conceded that the dispersion curve for dextrorotatory potassium cobaltioxalate is altogether analogous to the similar dispersion curve for dextrorotatory potassium chromioxalate, and that the dispersion curve for dextrorotatory potassium iridooxalate is altogether analogous to that for dextrorotatory potassium rhodi-oxalate, then the following interesting correlation is possible. (It should be noted that the order of the absorption bands is to a shorter wave-length on passing from cobalt through chromium and iridium to rhodium.)

* Inflexion mentioned above indicates approach to a maximum (anomaly or true anomaly).

Optically active potassium salt.	Dispersion.	"Sign" of rotation of complex salt.	Relative configuration deduced from dispersion.
Cobalti oxalate.*	True anomaly.	Lævo "*l*"	Give less soluble
*Chromi oxalate.**	True *anomaly* and anomaly (in negative region).	Lævo "*l*"	*strychnine* compounds of the general type
Iridio oxalate.	True anomaly.	Dextro "*l*"	*l*-strychnine +
Rhodi oxalate.	Anomaly (in negative region).	Dextro "*l*"	"*l*" complex.

* The lævorotatory compounds are considered for simplicity of treatment.

A point of further importance with regard to the enantiomorphism of the crystalline forms, which has been noted by Jaeger, is that lævorotatory potassium cobaltioxalate exhibits a right-handed trigonal bipyramid, whereas dextrorotatory potassium iridooxalate and dextrorotatory potassium rhodioxalate similarly exhibit a right-handed trigonal bipyramid. All three complex salts exhibit hemihedral forms of the same algebraic sign (+).

The dispersion data indicate that the relative configuration of the complex salts of cobalt, chromium, iridium, and rhodium may be denoted by the symbol "*l*," which is in accordance with Werner's law but opposed to Jaeger's conclusions.

The dispersion diagram * for these compounds of the same configuration is of considerable interest : with the movement of the absorption band into the violet, that part of the dispersion curve to the right of the band increases over a greater range of wave-length into the visible spectrum. The curves (direction, red to blue) all ascend to absorption bands in the positive region. From the diagram, which consists of a series of dispersion curves of a truly comparative series of active co-ordination compounds, one can realise the specific influence of the central atom on the dispersion, and further, the relationship of corresponding absorption bands to, and influence on, the dispersion. Comparison of this diagram with the dispersion diagram for the comparative series of complex triethylenediamine salts, as tabulated in the previous section, brings out the influence of the substituents and the comparative asymmetry of the molecule, just as in the case of the carbon compounds two series of the same relative configuration can be compared.

Cinchonine *l*-rhodimalonate is the less soluble salt and the isolated lævorotatory potassium rhodimalonate exhibits a maximum dispersion at λ 5800 in the negative region, at which wave-length there is no absorption band ; accordingly the compound is assumed to be of relative configuration "*l*." The substitution of three oxalyl for the malonyl radicals round the central atom results in a diminution of rotation in the region of anomaly, and actual crossing

of the zero axis is realised for the complex oxalate. Although the alkaloids used in the resolutions were different in the two cases of the isolation of the optically active complex malonate and of the oxalate, yet the isolated salts from the less soluble compound have the same relative configuration "*l*." Data given for potassium malonochromate are in full agreement: salt obtained, *l*-strychnine malonochromate-acid; dispersion, analogous to that of the corresponding complex oxalate; configuration, deduced from the dispersion, "*l*." The strychnine *l*-salt is anomalous in the negative region, but no conclusion can be drawn from this fact as to the configuration of the chromium complex. In the complex malonates, as in the other cases considered, the absorption band has moved to a shorter wave-length in passing from chromium to rhodium.

The researches of Jaeger and his collaborators have been of fundamental importance in deciding the relative configuration of co-ordination compounds.

Anomalous Rotatory Dispersion with Circular Dichroism.

Longchambon (*Compt. rend.*, 1924, **178**, 1828) has compared the rotatory dispersion of dextrorotatory potassium rhodioxalate in solution and in the crystalline state. The curves are similar, visual anomaly being shown in both cases by crossing of the zero axis and by maxima (for α and ρ) in the negative region. Crossing of the axis, however, has been displaced to a shorter wave-length (λ 5190) in the crystalline state. Longchambon considers that the rotatory dispersion in both cases may be represented by a *two*-term Bruhat equation, one term, the dispersion constant of which is negative, representing the anomalous rotatory dispersion at an absorption band near or in the visible region, and the second term, a low-frequency term, the dispersion constant of which is positive, representing the normal rotatory dispersion proceeding to a band in the near ultra-violet.

The rotatory dispersion of the co-ordination compound is analogous to that exhibited by 1:2-diphenyl-3-*l*-bornyl-imidoxanthide [*l*-bornyl *N*-thiobenzoyl-*N*-phenylthioncarbamate] (Tschugaev, *Ber.*, 1909, **42**, 2244; *Z. physikal. Chem.*, 1910, **74**, 503; *Ann. Chim. Phys.*, 1911, **22**, 137) and has been investigated quantitatively by Bruhat (*Ann. Physique*, 1915, **22**, 237). The measurements obtained are in agreement with a three-term equation

$$\alpha = \underbrace{\frac{D(\lambda^2 - \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2 + T^2\lambda^2}}_{\text{True Anomaly Term.}} + \underbrace{\underbrace{\frac{A}{(\lambda^2 - \lambda_1^2)}}_{\text{Low-Frequency Term.}} + \underbrace{\frac{B}{\lambda^2}}_{\text{High-Frequency Term.}}}_{\text{Anomaly.}}$$

The first term represents anomaly due to the absorption band in the green (λ 5240); D, T, and λ_0 were determined from the curve of circular dichroism, D being negative. A is positive; the second term represents normal positive rotatory dispersion exhibited in the visible region on proceeding to the band λ_1 3520 on the longer wave-length side of the band.

Bruhat found that, in order to obtain agreement between observed and calculated values, it was necessary to introduce the third (high-frequency) term, the constant B being negative. This term represents visible normal negative rotatory dispersion on proceeding to a band in the remote inaccessible ultra-violet region. λ_1 was deduced from the dispersion of the refractive index, A and B from rotatory dispersion.

This quantitative expression, involving data given by circular dichroïsm, variation of refractive index, and rotatory dispersion, is significant. The results indicate that (*a*) crossing of the axis is accompanied by circular dichroïsm; (*b*) the high-frequency term is negative, indicating a compound of relative configuration "*l*," which is in agreement with the mode of crossing the axis ($d\alpha/d\lambda$ negative); (*c*) crossing of the axis is on the longer wave-length side of the band and not at the band; (*d*) the rotatory dispersion does not proceed to $\pm \infty$ at the band; (*e*) the case is not analogous to the rotatory dispersion of tartaric acid, of which the anomaly is not accompanied by circular dichroism (Bruhat, *loc. cit.*) and is represented as the sum of two simple partial rotations, the characteristic frequencies being both in the ultra-violet; (*f*) the rotatory dispersion of the *l*-bornyl derivative can be referred to the superposition of three partial rotations: one represents true anomaly at the absorption band in the visible region, the other *two* are simple partial rotations, the characteristic frequencies of both being in the ultra-violet, and are characteristic of anomalous and potentially anomalous optically active, transparent compounds.

The phenomena exhibited by this compound appear to be similar in general character to those exhibited by methyl and ethyl *d*-bornyl xanthogenide and *l*-bornyl dixanthogenide (Tschugaev, *loc. cit.*; compare also derivatives of fenchyl alcohol). The compounds follow the rule with regard to the occurrence of anomalous rotatory dispersion and the relative configuration; for instance, the rotatory dispersion curve for the transparent *l*-menthyl ester of triphenylacetic acid exhibits a maximum in the negative region, that for *l*-menthol dithiourethane exhibits inflexion, maximum, and crossing of the axis from the negative to the positive region.*

* Maximum light absorption occurs at λ 5160, and crossing of the axis at λ 5280 (approx.).

Further, Tschugaev has pointed out with respect to certain of the above compounds "that in many cases the anomalous dispersion curves are shifted by the influence of temperature and by the nature of the solvent in the same direction as in the case of tartaric acid and its esters."

The borneol esters employed by Tschugaev were not contaminated with the corresponding but differently rotating *iso*borneol esters (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 988; Pickard and Littlebury, J., 1907, **91**, 1973).

Further consideration of the phenomenon of circular dichroïsm is deferred. On the above grounds it is considered that the dispersion data for dextrorotatory potassium rhodioxalate, both in solution and in the crystalline form, suggest the relative configuration "*l*."

Configuration and the Algebraic Sign of the Hemihedral Form.

A point of interest arising from the study of co-ordination compounds is whether the right- or left-handed (R.-H. or L.-H.) character of hemihedral crystals is, in general, directly related to the relative configuration of the constituent molecules. In the following scheme, d represents the density of the crystalline form, and ρ_D is the rotation per mm.

Compound.	$\frac{d\,[\alpha]_D}{100}$	ρ_D.	Character of crystal.	Configuration.	Difference of rotation (cryst. — soln.).
Quartz	—	+21·73°‡	L.-H.	"*l*"	—
l-Tartaric acid*	−0·12°	+11·4§	L.-H.	"*l*"	+11·52°
l-$NaKC_4H_4O_6$	−0·47	− 1·35§	R.-H.	"*l*"	− 0·88
l-$NH_4NaC_4H_4O_6$	−0·52	+ 1·55§	L.-H.	"*l*"	+ 2·07
l-$(NH_4)_2C_4H_4O_6$	−0·61	+ 8·9‖	L.-H.	"*l*"	+ 9·51
l-$Rb_2C_4H_4O_6$	−0·69	+10·24¶	L.-H.	"*l*"	+10·93
l-$Cs_2C_4H_4O_6$	−ve. rotn.†	+19	L.-H.	"*l*"	+ve. rotn.
Ammonium molybdomalate	+5	+32·3‖	L.-H.	"*l*"	+27·3
d-Camphor	+0·55	+ 0·65‖	L.-H.	"*l*"	+ 0·10
l-Asparagine	−0·06 × *d* (λ 5893)	− 6·2‖ (λ 5780)	R.-H.	"*l*"	−ve. rotn.
d-$K_3[Rh(C_2O_4)_3]$ (for λ 6400)	−1·3 (approx.)	− 9·5‖	R.-H.	"*l*"	− 8·2

* *l*-Tartaric acid and derivatives have been considered for simplicity.

† Exact data not available.

‡ Lowry.

§ Dufet, *J. Physique*, 1904, [iv], **3**, 757.

‖ Longchambon, *Compt. rend.*, 1922, **175**, 174; 1921, **173**, 89.

¶ Traube.

The following examples are important.

1. In quartz the asymmetry of the crystalline form has been

induced by the non-asymmetric silicon dioxide molecules striving after a tetrahedral arrangement of the oxygen atoms round the silicon atom.* The dispersion data indicate that the tetrahedral arrangement in left-handed quartz is of relative configuration "*l*." In the table the convention of chemists with regard to the taking of polarimetric measurements opposite to the direction of the propagation of the light is adhered to. In this case the molecules give rise to optical activity only while they are constituents of the crystal, *and the optical activity is induced by crystal structure* alone.

2. In the crystalline form, potassium rhodioxalate exhibits an increase of rotation in the negative region (to which region the compound belongs since it is of "*l*" configuration) and a displacement of the crossing of the axis to a shorter wave-length.

This difference of the dispersion curves in the two states could be interpreted by orientation producing distortion of the molecules in the crystalline state and so affecting the ratio of the positive *and negative dispersion constants; the molecules may occupy* a spiral arrangement in the crystal, and this arrangement may affect the magnitude of the rotation.

The crystalline symmetry of the oxalate ($L^3 \, . \, 3L^2$) is identical with the molecular symmetry indicated by Werner's stereochemical representation. Longchambon (*loc. cit.*) considers that all the molecules have a more or less perfect, parallel orientation; Burgers (*Proc. Roy. Soc.*, 1927, *A*, **116**, 553), however, concludes that the similarity of the dispersion curves in the two states is not due to a parallel, but may be partly due to the spiral, arrangement of the molecules in the crystal.

The algebraic sign of the hemihedrism is directly related to the relative configuration for the complex salt mentioned above. It is therefore considered that the movement in the rotatory dispersion is due to the superimposed effect of the spiral arrangement, accompanied by a slight distortion of the molecules themselves. This latter effect is similar to that produced by temperature, solvents, etc.

The dextrorotatory complex oxalate crystallises in the rhombic system with the symmetry of quartz and exhibits a single right-handed trigonal bipyramid; Jaeger (*loc. cit.*) states that a trapezohedral face is never present.

Asparagine and sodium potassium tartrate are further examples of compounds of relative configuration "*l*" associated with right-

* *Compare the case of lithium potassium sulphate* (*Burgers, loc. cit.*) *where* the oxygen tetrahedra are found to be regular.

handed forms. Using the convention of physicists, the algebraic sign of the rotation in the crystal and in solution as well as the crystalline form is +; this convention leads to simplicity in the tabulation of results.

The cases of quartz and the rhodioxalate are interesting examples showing, respectively, optical rotation induced in inactive molecules by crystalline structure, the active molecules then being arranged spirally, and rotation due to active molecules little influenced by crystalline structure although the active molecules are arranged spirally.

Tartaric acid presents a case where a spiral arrangement in the crystal may influence the rotatory dispersion, this spiral being due, not to the arrangement of the crystal molecules, but to the differences between the crystal and the chemical molecule. Astbury (*Proc. Roy. Soc.*, 1922, *A*, **102**, 506) has shown that the arrangement of the two tartaric acid molecules in the crystal unit produces through the hydroxyl groups an opposite spiral to that produced by the asymmetric carbon atoms.

The distortion effect of the molecules upon one another favours the negative dispersion coefficient, and the resulting crystal shape is opposite in stereometrical character to that of the molecules. On dissolution of the substance, the negative dispersion coefficient regains its normal value, visual anomaly resulting, and an explanation based on polymerisation is not necessary to account for the anomaly in solution, since rotatory dispersion both in the crystal and in solution is essentially molecular, the effect of crystal structure being analogous to the effect of solvents.

Other cases are afforded by sodium ammonium tartrate, and ammonium, rubidium, and cæsium tartrates.

In the majority of the tartrates it is the left-handed crystal which is associated with a compound of relative configuration "*l*," and in the above cases, whenever there is a change of sign in rotation from solution to crystal, the relative configuration is indicated, *e.g.*, *left*-handed sodium ammonium "*l*"-tartrate has *negative* rotation in solution, and *positive* in the crystal. The data are, however, too restricted to support a generalisation.

Ammonium molybdomalate and camphor are two interesting examples of compounds of relative configuration "*l*" exhibiting positive rotations both in solution and in the crystalline form. The positive dispersion coefficient of the molecules, distorted but exhibiting the shape of a molecule of "*l*" configuration, has persisted in and, in the case of the malate, has been enhanced by crystal structure, the crystals being of opposite stereometrical character to that of the relative configuration of the molecules.

This involves the point that right-handed "*l*"-asparagine is in crystalline structure more closely related to *right*-handed sodium ammonium tartrate than to the *left*-handed tartrate, even though "*l*"-asparagine and sodium ammonium *d*-tartrate are of opposite relative configuration (see table).

Ostromisslensky (*Ber.*, 1908, **41**, 3035) observed that an inactive supersaturated solution of sodium ammonium *d*- and *l*-tartrates, when inoculated (at 6°) by a nucleus of *l*-asparagine, deposited exclusively the *right*-handed variety, but a supersaturated solution of sodium ammonium *d*-tartrate does not deposit crystals when inoculated with a nucleus of the *l*-tartrate (Gerez, *Compt. rend.*, 1866, **63**, 843). The enantiomorphous nucleus has an exclusive directional influence.

Summary.

1. Optically active co-ordination compounds exhibit anomaly and true anomaly, the former indicating the relative configuration.

2. *The configuration as deduced from dispersion data is in agreement with Werner's law.*

3. The algebraic sign of the hemihedral form of the co-ordination compound considered indicates the relative configuration, but no generalisation can be made at present.

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CCXXIII.—*The Study of Moving Flames.*

By WILLIAM PAYMAN.

DURING researches on the propagation of flame in gaseous mixtures methods of photography have been developed in the laboratories of the Safety in Mines Research Board which depend upon the abrupt change in the optical properties (refractive index) of a gas mixture at the surface of a flame passing through it. A method depending upon the same principle has recently been described by A. G. White (this vol., p. 1159). It is therefore considered desirable to place on record brief descriptions of the two methods which we have been using during the past few years. Such methods should prove of value to other workers.

It was first suggested by Foucault ("Annales de l'observatoire imp. de Paris," Tome V) that changes in the optical properties of glass caused by flaws could be followed by the refraction of a beam

of light passing through the glass. This suggestion was applied to the similar problem of refraction in air, by Töpler in his Schlierenmethode (*Ann. der Phys.*, 1867, **131**, 33) and by Dvŏrák in his "shadow method" (*Ann. der Phys.*, 1880, **9**, 502). Both these investigators recorded the effects they obtained photographically.

The methods developed in these laboratories for determining the speeds of flames and examining their mode of propagation are based on those of Töpler and Dvŏrák. Two cameras are in use. The first, which we have designated the "flame-speed camera," utilises Dvorák's method. It is of limited application, being of chief use for the photography of slowly moving and feebly actinic flames. The second, which we term the "wave-speed camera," is based on Töpler's method and has been used with success for the photography of both slowly and rapidly moving flames, whether feebly or strongly actinic, as well as of movements of invisible compression waves which are sent out by rapidly burning mixtures. The "wave-speed camera" has been described in detail in Safety in Mines Research Board Papers Nos. 18 and 29, 1926.

Both cameras make use of a revolving drum around which the photographic film or paper is stretched, and special means of synchronising the time of exposure with the moment of passage of flame across the field of view have been designed. Both cameras have been arranged so that a direct photograph of the flame can be obtained of exactly the same size as the refraction photograph, when the flame is sufficiently actinic. The two photographs of one explosion are often of great assistance to each other in interpreting the results obtained.

The flame-speed camera. With the flame-speed camera the method used differs but little from that described by White. A diverging beam of light from a powerful mirror-arc lamp is passed through a small orifice (to provide a point source of illumination) and through the explosion-vessel containing the mixture to be inflamed, whence it passes to the camera drum. In order to obtain a photograph of a sufficient length of explosion vessel without using too wide a film, a simple plano-convex condenser, 20 cm. in diameter, is placed between the explosion vessel and the photographic paper, so that a reduction to approximately one-quarter natural size is obtained.

The wave-speed camera. The wave-speed camera is more complicated, but it has the advantage that it can be used for the photography of all kinds of flames and shock-waves, and may be used in an undarkened room. Where the flame is sufficiently actinic it is recorded on the film simultaneously with the refraction photo-

graph. A converging beam of light is used—namely, the beam from a mirror-arc lamp reflected by means of a concave mirror. This reflected beam is focussed on the lens of the camera, a diaphragm on which serves to separate refracted from non-refracted light.

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155
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